PHOTOCHEMICAL REACTIONS OF TITANIUM DIOXIDE

BY

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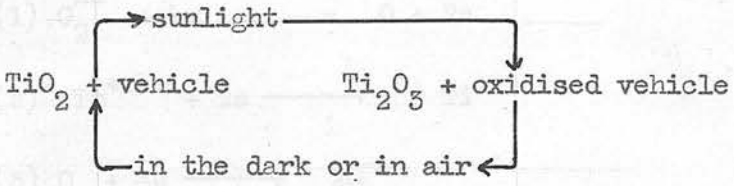
INTRODUCTION

The extremely high degree to which titanium dioxide reflects light has led to its large scale use as a pigment in the paint and paper industries and as a delustering agent for artificial fibres in the textile industries. Although ideal in physical properties titanium dioxide has adverse chemical properties in such respects that its use is accompanied by the flaking of paints and the tendering of fabrics, actions largely induced on exposure to light. (1, 2, 3, 4, 5).

Before MacKenzie and Kennedy (1950) most of the research into this problem was done on paints and fabrics themselves or on model systems that retained most of the complexities associated with paints and fabrics.

Most of the earlier views held in the degradative photo-properties of titanium dioxide envisaged a reduction of TiO_2 to Ti_2O_3 with subsequent re-oxidation of Ti_2O_3 to TiO_2. For example, A.E. Jacobsen's (1) work led him to the following cyclic scheme:-



Renz (6) also working along similar lines claimed to have identified CO_2 as a product from the action of light on the system:- TiO_2 + glycerol + light, and that the darkening of the oxide was due to reduction of the titanium dioxide. Ruben (7), however, favoured the view of the formation of a higher oxide. Jacobsen supports his view by claiming to have identified αTi_2O_3 by electron diffraction as an end product from the illumination of the paste of titanium dioxide and glycerol. According to Jacobsen a number /

number of media are capable of being oxidised in this manner, namely:- glycerol, aqueous solutions of tartaric acid, mandelic acid and stannous chloride.

Goetz and Inn (8) have interpreted the darkening of titanium dioxide on exposure to U.V. light in presence of silver nitrate, Forland (9), as a reduction of Ag^{+} to Ag.

Weyl and Forland (10) proposed the oxidation to Ag^{++} in the basis of the following observations:-

$$TiO_2 + Ag^{+} \xrightarrow[\text{hydrazine sulphate + ammonia}]{\text{reduction}} TiO_2 + Ag.$$

darkening

$$\xrightarrow{U.V.} TiO_2 \text{ (reduced)} + Ag^{+} \xrightarrow{U.V.} TiO_2 \text{ (further reduced)} + Ag^{++} \text{ (AgO)}$$

fading — strong darkening

and consider that photo-oxidations at the surface of the oxide stem from the photolysis of the oxide and that oxidation proceeds via liberated atomic oxygen. In air the process is regarded as reversible.

$$(1)\ O_2^{--} + h\nu \longrightarrow O + 2e$$

$$(2)\ 2Ti^{++++} + 2e \longrightarrow 2\,Ti^{+++}$$

$$(3)\ O_2 + 4e \longrightarrow 2O^{--}$$

Bleaching of the dye chlorazol sky blue deposited (11,12) on titanium dioxide can be effected in vacuum, and in oxygen, both under the action of light ($\lambda < 4000\text{Å}$). The colour changes observed on the oxide closely resemble those which are apparent on oxidation of the dye by acid permanganate and it is likely that the fading on the surface of the oxide is an oxidation process caused by the actionoof light. At present it would appear that the fading in vacuo is also an oxidation process but the results of the experimental

work /

work about to be described indicate that it may be due to reduction of the colour producing azo groups:-

$$X\text{-}N = N\text{-}Y + 2H^{+} + 2e \longrightarrow X\text{-}\overset{H}{N} - \overset{H}{N}\text{-}Y$$

the product being stable on illumination in presence of oxygen.

Attempts by Goodeve (11) to measure oxygen liberated during illumination of titanium dioxide in vacuo proved unsuccessful and it was shown by MacKenzie (12) that illumination of titanium dioxide in oxygen resulted in an uptake of oxygen. This suggests that the titanium dioxide is deficient in oxygen and that during the illumination such photosorbed oxygen may be utilised by oxidisable materials such as paint films and textile fibres.

Kennedy (13) continued the work done by MacKenzie and examined the characteristics of the oxygen uptake on variously prepared and pre-treated titanium dioxide samples in a solid-gas system thermostated at 25°C. Samples of titanium dioxide were deposited as a slurry with acetone on the inside face of the reaction vessel and dried out into a film by evaporation. Evacuation of the titanium dioxide film for a minimum period of four days at 10^{-5} mm. was applied before admitting oxygen to 50 mm. and illuminating with light of 3650Å. Pressure decrease measurements were then made in a closed volume system.

The amount and rate of the oxygen uptake was found to vary with each sample and to vary again with its pre-treatment. Rutile was found to be less active than anatase while chromium treated samples were found to be less active than untreated samples. Heating in an atmosphere of H_2, CO, and O_2 at 400°C had little effect upon the oxygen uptake, but heating at 800°C was found /

found to have reduced the activity considerably, this being no doubt due to sintering with subsequent loss of surface area.

The rate of oxygen uptake was shown to be dependant on the following variables:-

(1) Oxygen Pressure

(2) Intensity of Light

(3) Wavelength of Radiation

(4) Oxygen Uptake

(5) Temperature

(1) Oxygen Pressure

The rate of oxygen uptake relative to a fixed amount of oxygen uptake ΔO_2 (i.e., relative rate), was found to be dependant upon $P_{O_2}^{\frac{1}{2}}$ suggesting a Langmuir dissociative adsorption of oxygen, with adsorbed oxygen atoms as being responsible for determining the rate of the uptake. The relationship observed was:-

$$\frac{K\left(\frac{dO_2}{dt}\right)_{\Delta O_2}}{1 - K\left(\frac{dO_2}{dt}\right)_{\Delta O_2}} = K^1 \Delta P_{O_2}^{1/2}$$

or

$$\left(\frac{dO_2}{dt}\right)_{\Delta O_2} = \frac{K^1 \Delta P_{O_2}^{1/2}}{K\left(1 + K^1 \Delta P_{O_2}^{1/2}\right)}$$

(2) Intensity of Light

The relative rate of oxygen uptake was found to vary directly with the intensity of incident light (I = 3650Å).

$$\left(\frac{dO_2}{dt}\right)_{\Delta O_2} = K \times I_{(3650\text{Å})}$$

(3) Wavelength of Light

On a quantum basis light of wavelength less than 4000Å was found to be the most effective.

Table I

Relative Rate	λ Å
1.00	3650
0.42	4050
0.065	4360

(4) Oxygen Uptake

The rate at constant temperature, intensity of illumination and oxygen pressure was found to vary with the amount of the oxygen uptake. Kennedy found in the initial stages of the oxygen uptake that a parabolic relationship existed between the time of the illumination and the uptake.

$$(\Delta p + \Delta p')^2 = (Kt + (\Delta p')^2)$$

Where Δp was the observed oxygen uptake (pressure decrease) and K and $\Delta p'$ were constants.

In the final stages an exponential law was obeyed:-

$$\frac{d\Delta p}{dt} = K(\underset{\infty}{\Delta p} - \Delta p)$$

which allowed extrapolation to find the ultimate amount of oxygen uptake $\underset{\infty}{\Delta p}$. $\underset{\infty}{\Delta p}$ corresponded to 50×10^{-6} moles/gm. for the commercial samples and 300 to 500×10^{-6} moles/gm. for the laboratory prepared samples of titanium dioxide, such data illustrating the higher activity of samples prepared at low temperatures, i.e. at less than 150°C.

(5)/

(5) Temperature

The rate of uptake of oxygen was shown by MacKenzie to be subject to a temperature coefficient corresponding to +5 K cals/mole and is therefore not a true photochemical process. There are, however, numerous factors associated with the oxygen uptake that are temperature dependant, one of them being the presumed Langmuir dissociative adsorption of oxygen.

Kinetics of the Uptake

Kennedy considered that the overall photo-process was an irreversible chemisorption of the oxygen with electron transfer from the oxide to the oxygen atoms, the electrons being made available on the absorption of light within the first absorption band of the solid. The scheme he proposed postulated the existence of two types of surface site where oxygen may be chemisorbed. On both types chemisorption takes place with the donation of electrons from the titanium dioxide crystal to the oxygen, to form the chemisorbed species O^-. At sites A reversible chemisorption takes place at 25°C in accordance with the Langmuir type isotherm for dissociative adsorption:-

$$\theta = A\ P_{O_2} \qquad \theta = \text{fraction of surface covered by } (A^+ + O^-)$$

Here equilibrium is reached rapidly.

$$\tfrac{1}{2}O_2 \text{ gas} + A = (A^+ + O^-) \ldots\ldots\ldots\ldots\ldots \text{rapid} \qquad (1)$$

Chemisorption on sites B occurs at 25°C only on illumination with light of wavelength $< 4000\text{Å}$ and is virtually irreversible. The number of B sites is much greater than the number of A sites.

A small fraction of the electrons in the conduction band then become trapped at empty A levels freeing the reversibly chemisorbed O^- for diffusion

across/

across the surface.

$$(A^+ + O^-) + e = (A + O^-) \text{.....rapid} \quad (2)$$

with only a very small fraction of empty A levels becoming occupied by electrons from the conducting band.

The process of electron trapping and release is fast and reaches equilibrium almost instantaneously. The number of diffusing species, i.e. the number of $(A + O^-)$ is at any instant proportional both to the number of electrons in the conduction band and to the number of A sites occupied by oxygen, i.e. $(A^+ + O^-)$.

The reversibly chemisorbed oxygen diffuses across the surface to the B sites, where rapid combination takes place with the positive holes of the valence band to form an irreversibly chemisorbed species.

$$(A + O^-) + B \longrightarrow A + (B + O^-) \text{.....slow diffusion} \quad (3)$$

$$(B + O^-) + \oplus \longrightarrow (B^+ + O^-) \text{ .....rapid} \quad (4)$$

Systems other than titanium dioxide and oxygen were also investigated by Kennedy. No evidence of photochemical reactions with H_2 or CO was observed nor was there any observed reaction with adsorbed molecules such as mandelic acid deposited by evaporation from solution in acetone. There was, however, a large pressure decrease in illuminating titanium dioxide in presence of nitric oxide. From pressure measurements the photo process appeared to be the formation of one N_2O molecule from four NO molecules. No evidence of any other nitrogen compound was found and the chemical process given by Kennedy in conformity with pressure measurements was:-

$$\underset{\text{gas}}{4NO} \longrightarrow \underset{\text{adsorbed}}{(N_2O_3)} + \underset{\text{gas}}{N_2O}$$

The kinetics of this process were very similar to the uptake of oxygen/

oxygen. A slow small dark uptake of NO was usually observed on admitting the gas to the reaction vessel. The rate of this dark process decayed rapidly.

The amount of N_2O produced on illumination was approximately one quarter of the NO uptake with an experimental variation more than was consistent with the accuracy of the measurements.

The relative rate of the uptake of NO was found to be of the type:-

$$\frac{(dNO)}{(dt)}_{\Delta NO} = K \Delta P_{NO}^{1/2}$$

and does not necessarily imply dissociative adsorption of NO.

Among the various objects of this present work is the establishing of the common factors between oxygen and nitric oxide uptakes, and both oxygen-titanium dioxide and nitric oxide-titanium dioxide systems have been further investigated. In addition, processes occurring between titanium dioxide and ammonia and also ammonia-oxygen mixtures have been examined.

DEGREE OF HYDRATION OF TITANIUM DIOXIDE

The extent to which oxygen is taken up on titanium dioxide is 500×10^{-6} moles oxygen/gm. for the more active laboratory prepared samples. The laboratory prepared samples are by nature largely hydrated since water will not be removed entirely below temperatures of 900 to 1000°C.

The dehydration of titanium dioxide gels was studied by many workers (14) who found that the water content of titanium dioxide gel varied according to the drying process. A. Demoly (14) found that the drying of the gel precipitated from a hot aqueous solution gave, when dried in vacuo, a product corresponding to $3TiO_2.2H_2O$ (= 15% H_2O) and when dried at 140°C a water content of 12%. J. Tuttscheff (14) found that drying at 120°C gave a water content of 22.15 to 22.46% and at 140°C a water content of 12.95%. After drying for several weeks in air, V. Merz (14) obtained a product with 18.48 to 19.22% water and on drying over conc. H_2SO_4 the overall composition after 12 hours was $TiO_2.H_2O$ and after 6-10 weeks $2TiO_2.H_2O$. He also examined the effect of drying in air at various temperatures:-

Table II

Drying Temp.	60-70°C	110°C	120°C	130°C	150°C	170°C
% Water	9.45-10.91	6.83	5.17-5.46	5.05-5.53	4.22-4.46	4.17-4.53
Ratio $TiO_2:H_2O$	-	3:1	4:1	-	-	5:1

Table II shows that the rate of loss of water is greater between 60°C and 100°C than between 100°C and 170°C. The drying of gels was further investigated by Latty (15), who observed as Merz did that the rate of dehydration was greatest at the lowest temperatures but also showed that dehydration occurred up to 900°C. Since the laboratory prepared samples used by Kennedy and Mackenzie were never heated much above 100°C, it is to be expected /

expected that they contained a large number of hydroxyl groups and water molecules, on the surface and within the crystal itself. Real information on the part played by water and hydroxyl groups on the titanium dioxide surface is lacking and part of this work is directed towards this end. Yu. P. Solonitsyn (16) has shown that the hydroxyl groups on silica gel play an important part in the photosorption of oxygen with light of wavelength less than 2500Å. The primary process is assumed to be the liberation of OH groups by photolysis from the surface:-

$$-\overset{|}{\underset{|}{Si}} - OH \xrightarrow{\lambda < 2500\text{Å}} -\overset{|}{\underset{|}{Si}}\cdot\cdot\cdot\cdot + OH$$

the free valence produced then becoming a site for oxygen sorption and the free hydroxyl groups combine to produce hydrogen peroxide. It is doubtful if this occurs with titanium dioxide since any attempt to identify hydrogen peroxide has been unsuccessful.(12). Aqueous suspensions of titanium dioxide will liberate iodine from KI but measurement of the amount of iodine liberated is variable as the end point is fugitive (13). The same is found to occur with antimony oxide (17), and it may well be that the solid in suspension catalyses the oxidation of HI to H_2O and I_2 with dissolved atmospheric oxygen and that the rate of oxidationoof HI is dependant on the rate of solution of atmospheric oxygen. Markam et al (17) have claimed to have found H_2O_2 as a product on the illumination of antimony oxide (rhombic Sb_2O_3) in an oxygenated aqueous suspension, a reaction already well established for ZnO (18). This, then, is the only evidence that suggests the possibility of the production of H_2O_2. The liberation of I_2 from KI can also be explained by the reaction of OH radicals which produce H_2O and I_2 from acidified KI.

(1) /

(1) $O + H_2O \longrightarrow 2OH$

(2) $OH + HI \longrightarrow H_2O + \frac{1}{2}I_2$

The atomic oxygen having been produced in some way between the interaction of light, oxygen molecules and titanium dioxide with reaction 2 occurring in preference to reaction 3:-

(3) $2OH \longrightarrow H_2O_2$

MacKenzie has shown the existence of a very highly active oxidising agent confined to the immediate vicinity of illuminated damp titanium dioxide in a flow of oxygen. This is not likely to be H_2O_2 as the oxidising effect would be more widespread:-

Work by Walker (19) on zinc oxide "hyperfine" (a brick-red powder prepared by the pyrolysis of zinc ammonium carbonate at 250°C) has shown photo-properties in respect of oxygen similar to titanium dioxide. Experiments on the illumination of such ZnO have also shown a reaction with NO:-

$$3NO + e \xrightarrow{\lambda < 4000\text{Å}} N_2O + NO_2^-$$

and the extent of the nitric oxide uptake was in simple proportion to the uptake of oxygen:-

$$\Delta NO : \Delta p_{O_2} = 2:1$$

This immediately suggests that the two processes are very similar and it could well be that zinc oxide (as well as titanium dioxide) contains a specified number of sites which are excited by the action of light and in the activated state are responsible for the photochemical properties.

It is believed that from the photochemical reactions now to be reported some conclusions can be drawn as to the number and nature and the part played by such sites of adsorption.

Structure of Solids (20)

Solids can be divided into two general classes, the amorphous (non-crystalline) and the crystalline.

Since the titanium dioxide is crystalline the amorphous class can be excluded from this short discussion. Crystalline solids are subject to a number of imperfections occurring in their lattices. They can be classified into various types.

(a) Schottky Defects.

(b) Frenkel Defects.

(c) Non-stoichiometry.

(d) Dislocations.

In an ideal two-dimensional lattice the structure can be illustrated as follows:-

A^+ B^- A^+ B^- A^+ B^- A^+ B^-

B^- A^+ B^- A^+ B^- A^+ B^- A^+

A^+ B^- A^+ B^- A^+ B^- A^+ B^-

B^- A^+ B^- A^+ B^- A^+ B^- A^+

(a) Schottky defects can arise with A^+ and B^- ion vacancies.

A^+ B^- A^+ B^- A^+ B^- A^+ B^-

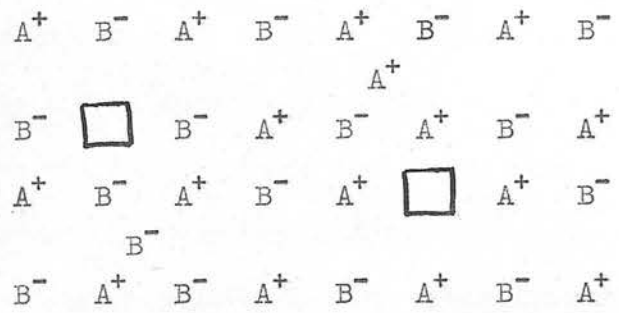
B^- A^+ $\square$ A^+ B^- A^+ B^- A^+

A^+ B^- A^+ B^- $\square$ B^- A^+ B^-

B^- A^+ B^- A^+ B^- A^+ B^- A^+

(b)/

(b) Insertion of interstitial ions in the neighbourhood of these vacancies give rise to Frenkel Defects:-



In addition the interstitial ions in the Frenkel Defects need not be, in this case, A^+ amd B^- but A^+ and C^- or B^- and D^+ or C^- and D^+, i.e. different ions. Should they be of a different valency from A and B, the interstitial ions will be centres of electropositivity or electronegativity and may give rise to semiconductivity (impurity semiconductors).

A direct result of ion vacancies is non-stoichiometry. This occurs when one ion vacancy occurs more than the other and may be one reason why oxygen is taken up on some oxides. The ease and irreversibility with which it occurs on titanium dioxide would suggest non-stoichiometry on the surface, i.e. an excess of Ti ions.

Dislocations occur during the formation of crystals, i.e. when crystallites combine together. The more rapid is the formation, the more is the extent of dislocation. In the rapid hydrolysis of $TiCl_4$ to form $Ti(OH)_4$ the $Ti(OH)_4$ formed, gradually undergoes dehydration with the formation of insoluble hydrated titanium dioxide. The rapidity of the process must lead to a high degree of dislocation in the crystalline structure. X-ray powder photographs of the hydrolysed specimens prepared in this manner give very diffuse diffraction bands in agreement with a dislocated and disordered crystal lattice structure (29). Interstitial ions of different valency, Ti^{+++}, may be introduced into the lattice from the hydrolysis of $TiCl_3$ which may occur from $TiCl_4$ before it is hydrolysed and it is then possible that the uptake of oxygen may be oxidation of inter-

stitial Ti^{+++} to Ti^{++++}. Some support for this possibility will be looked for in discussing the experimental results.

SEMICONDUCTIVITY AND CHEMISORPTION (22)

Since the oxygen photosorbed on titanium dioxide is irreversibly adsorbed, it may be concluded that the process involved is one of chemisorption.

It is the valency forces of the solid surface of the adsorbate which control the chemisorption and one has to seek a relationship between the electronic and the geometric configurations of the system as it moves from its initial to its final state through recognisable intermediates.

The adsorbants may be classified into three main types:-

(1) Metals

(2) Semiconductors

(3) Insulators

(1) Metals chemisorb or activate (render active catalytically) one or more of the simple molecules H_2, N_2, O_2, CO even at liquid oxygen temperatures. They can be classified into two types, d-type and s,p-type, according to whether they have low unfilled d orbitals and those without such orbitals.

(2) Semiconductors: Superposition of the orbital classification upon the more usual semiconducting types gives the following groups:-

n-type	$n_{s,p}$ - ZnO	n_d - V_2O_5
intrinsic	$i_{s,p}$ - Si,Se	i_d - CnO, Fe_2O_3
p-type	$p_{s,p}$ - none	p_d - NiO

Like s,p metals, $i_{s,p}$ semiconductors are relatively inert towards all gases except oxygen. Only n-type oxides chemisorb hydrogen readily, but some transition oxides (e.g. Cr_2O_3) appear to be more active than any $n_{s,p}$-type oxide in hydrogen-deuterium exchange. In oxygen reactions, the most active oxides are the p_d-type, the less active but more selective are the n_d-type, and the least active are $n_{s,p}$-type.

(3)/

(3) Insulators: All oxides, simple or mixed, drawn from groups 2 to 4 of the short periods. The cations are in their highest valency state so that the solids have only marginal semiconductivity ($n_{s,p}$-type). Slow hydrogen and oxygen exchanges are only catalysed above 350°C. Pure stoichiometric TiO_2 would belong to this group.

Titanium dioxide has a high resistance indicative of an insulator and is not appreciably affected by oxygen in the dark. Under the action of light ($\lambda < 4000\text{Å}$), and in vacuo, however, semiconductivity is observed (see experimental section) and is very much greater in magnitude than one would expect from the marginal $n_{s,p}$-type. It therefore remains to find out why semiconductivity occurs. Perhaps a clue may be obtained by looking at the electronic configuration of titanium. In the ground state titanium has the form(23):-

(Argon) $3d^2$.....$4s^2$ (partially filled 3d orbitals)

and since it forms tetravalent compounds the $3d^2$ electrons must be elevated to the 4p level:-

(Argon).....$4s^2 4p^2$ (unfilled 3d orbitals)

to give a configuration similar to carbon which is borne out by the physical similarity of their tetrachloride compounds. In titanium dioxide the $4s^2 4p^2$ electrons will have paired spins with four electrons of the four neighbouring oxygen ions resulting in an electronically balanced and stable crystalline lattice structure. It is difficult to visualise the production of current carriers from stoichiometric titanium dioxide on this simple basis. Some other factor, e.g. dislocations or other non uniformity must be responsible. Even if the surface titanium ions were linked to OH groups then ionisation by light adsorption:-

Ti/

$$-\overset{|}{\underset{|}{Ti}}-OH \xrightarrow{h\nu} -\overset{|}{\underset{|}{Ti^{+}}} + OH^{-} \qquad (1)$$

as with silica gel (16), would result in the production of H_2O_2:-

$$OH^{-} + O \longrightarrow O^{-} + OH \qquad (2)$$

$$2OH \longrightarrow H_2O_2 \qquad (3)$$

the $-\overset{|}{\underset{|}{Ti^{+}}}$ becoming the site for oxygen sorption. Since no definite evidence of H_2O_2 has been found this scheme must be discarded unless any H_2O_2 formed is catalytically decomposed by some other mechanism.

A possible source of electrons would be impurity centres which must exist to a reasonably large extent to account for the magnitude of the oxygen uptake as found by Kennedy.

McTaggart and Bear (24,25) have shown phototropic effects to occur in titanium dioxide containing traces of impurity metals such as iron, nickel chromium and copper, when illuminated with U.V. light. The conclusions McTaggart and Bear suggested were:-

(1) The impurities were adsorbed in the surface in such a way that the nature of the bonding rendered the impurity stable in the reduced form.

(2) On irradiation, oxygen is liberated from the TiO_2 which oxidises the impurity to a higher state.

(3) On cessation of irradiation the higher valence form of the impurity reverts to the lower form. (A process which takes minutes or weeks to occur and may be accelerated by heating).

(4) The rapid reversal of colour obtained when irradiated samples are heated at a relatively low temperature, may be the result of activation, in which the change of valence is accelerated.

(5) The presence of water molecules plays a decisive part in the process; this /

this may be due to their action with oxygen liberated from the titanium dioxide, or to their entering into the bonding between impurity and host oxide.

Their theory suggests that if the necessary properties of the host oxide are (a) that of giving oxygen when irradiated by light of a suitable wavelength and (b) the formation of suitable bands with impurity oxides, there should be other host oxides capable of giving rise to phototropic effects. Such other host oxides have been found (25).

Since only Analar grade materials, subjected to further purifications were used by Kennedy and MacKenzie in their preparations of titanium dioxide, it is regarded as likely that no foreign materials, such as those of McTaggart and Bear, could have been present. How, then, could "impurities" be introduced? In the light of the work of McTaggart and Bear it now seems reasonable to consider the possibility of surface sorbed trivalent titanium ions.

If some trivalent titanium were present, in the $TiCl_4$, on hydrolysis $Ti(OH)_3$ would be formed and therefore could be adsorbed on the surface of the $Ti(OH)_4$.

A trivalent titanium ion has a lone 3d electron:-

$$Ti^{+++} = (Argon)\ 3d^1 \ldots\ldots\ldots\ldots (+\ 4s^2 4p^1)$$

in its electronic configuration and photo electric effects might be induced by the elevation of this electron to a conduction band. The uptake of oxygen on illumination might then be due to some oxidation process where the surface sorbed trivalent titanium is converted to the tetravalent state. This could explain the irreversibility of the photo-uptake of oxygen.

The presence of ions of a lower valency would result in semiconductivity (n_d-type). A section of the experimental results will be devoted to the examination of this.

Some /

Some information on the part played by water molecules will be looked for since McTaggart and Bear have stated that their presence is necessary for phototropic effects to occur between host oxides and surface sorbed impurity ions in their lower valence state.

Only one preparation of titanium dioxide was used throughout the experimental work in the hope of correlating the various photochemical reactions on a quantitative basis and thereby deriving some information as to the nature of the surface photo-active sites.

APPARATUS (See figs. 1, 2 and 3)

The apparatus was designed and built from soda glass tubing with the following purposes in mind:-

(a) High vacuum system for the exclusion of air and removal of adsorbed substances from titanium dioxide samples and also to facilitate gas handling.

(b) Subsidiary system for evacuation and pre-treatment of titanium dioxide films.

(c) Reaction site thermostated at 25°C.

(d) Light source to induce photochemical reactions.

(e) Bourdon guage system for measuring accurately small pressure changes normally at a total pressure of approximately 50 mm.

(f) Gas reservoirs with associated leads and manometers to introduce required amounts of gas to the reaction vessel.

(g) Cold traps for isolation of condensible products (from photochemical reactions).

(h) Subsidiary analysis systems for identification and measurement of the reaction products.

(i) Suitable system for electrical conductivity measurements.

(a) High vacuum system. A two stage mercury diffusion pump was backed by an Edwards Rotary oil pump. Between the high vacuum line and the mercury pump a cold trap was maintained at liquid oxygen or nitrogen temperatures (-183 to -196°C). A second cold trap between the two pumps prevented mercury vapour from entering the oil pump. The internal pressure could thus be reduced to 10^{-5} mm of mercury as measured by a McLeod Guage. Taps and ground glass joints were lubricated with Apiezon L grease.

(b) A separate system enabled films to be evacuated and pre-treated before transferring to the reaction site. During transfer the reaction vessels were filled/

Fig 1

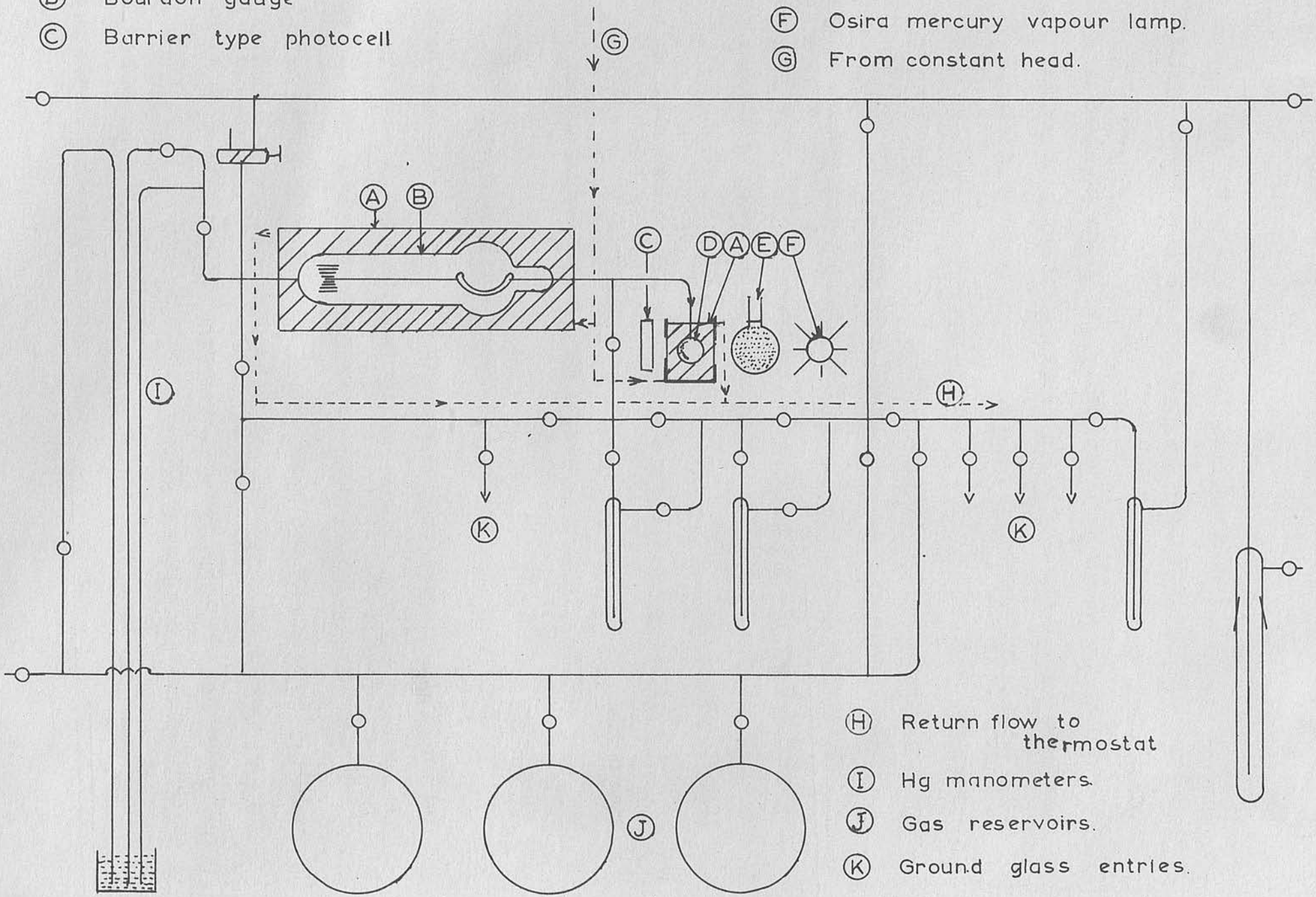
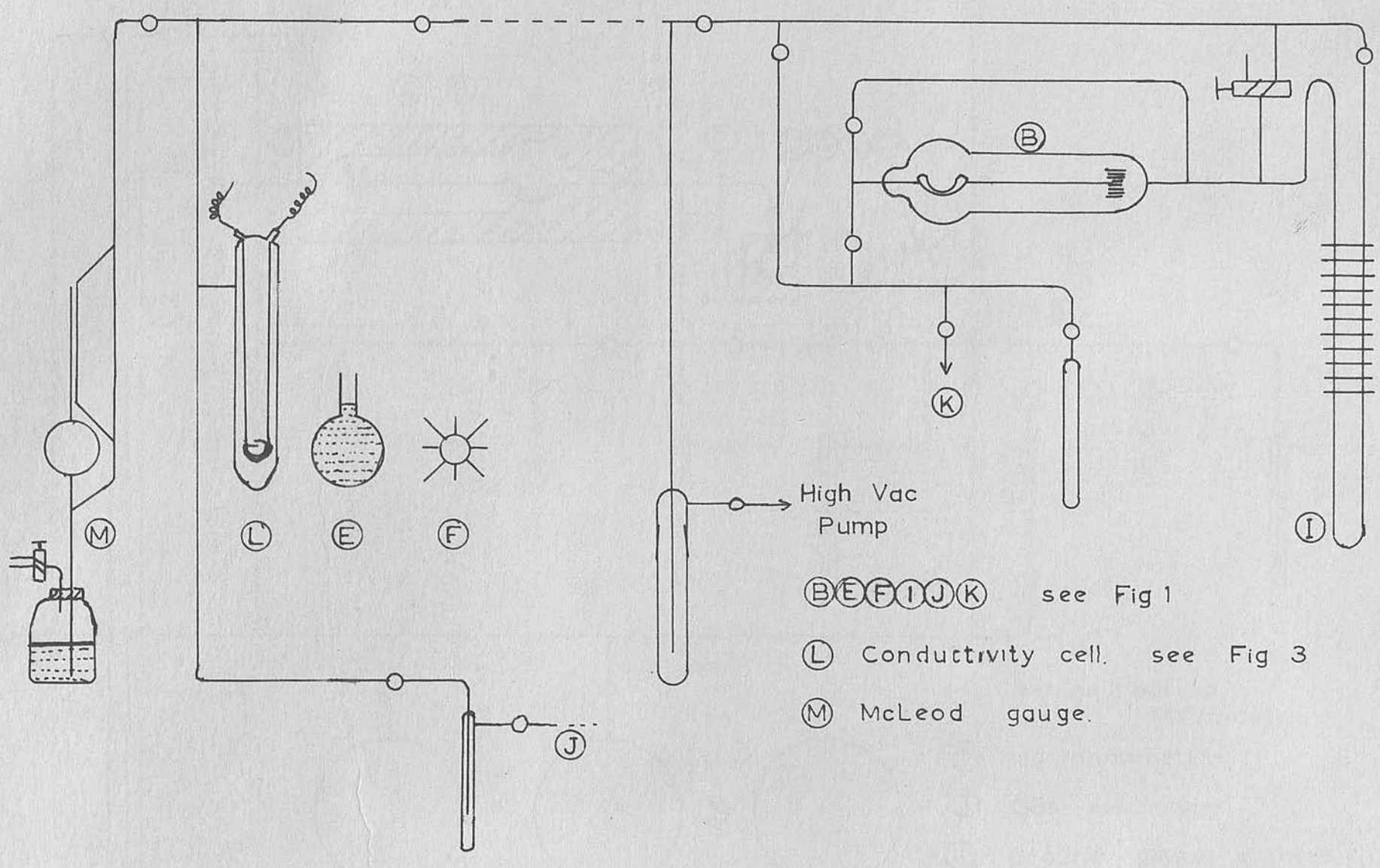

Ⓐ Constant temperature water jackets 25·0°C.
Ⓑ Bourdon gauge
Ⓒ Barrier type photocell
Ⓓ Reaction vessel.
Ⓔ $CuSO_4$ filter & condenser lens.
Ⓕ Osira mercury vapour lamp.
Ⓖ From constant head.
Ⓗ Return flow to thermostat
Ⓘ Hg manometers.
Ⓙ Gas reservoirs.
Ⓚ Ground glass entries.

Fig 2



(B)(E)(F)(I)(J)(K) see Fig 1

(L) Conductivity cell. see Fig 3

(M) McLeod gauge.

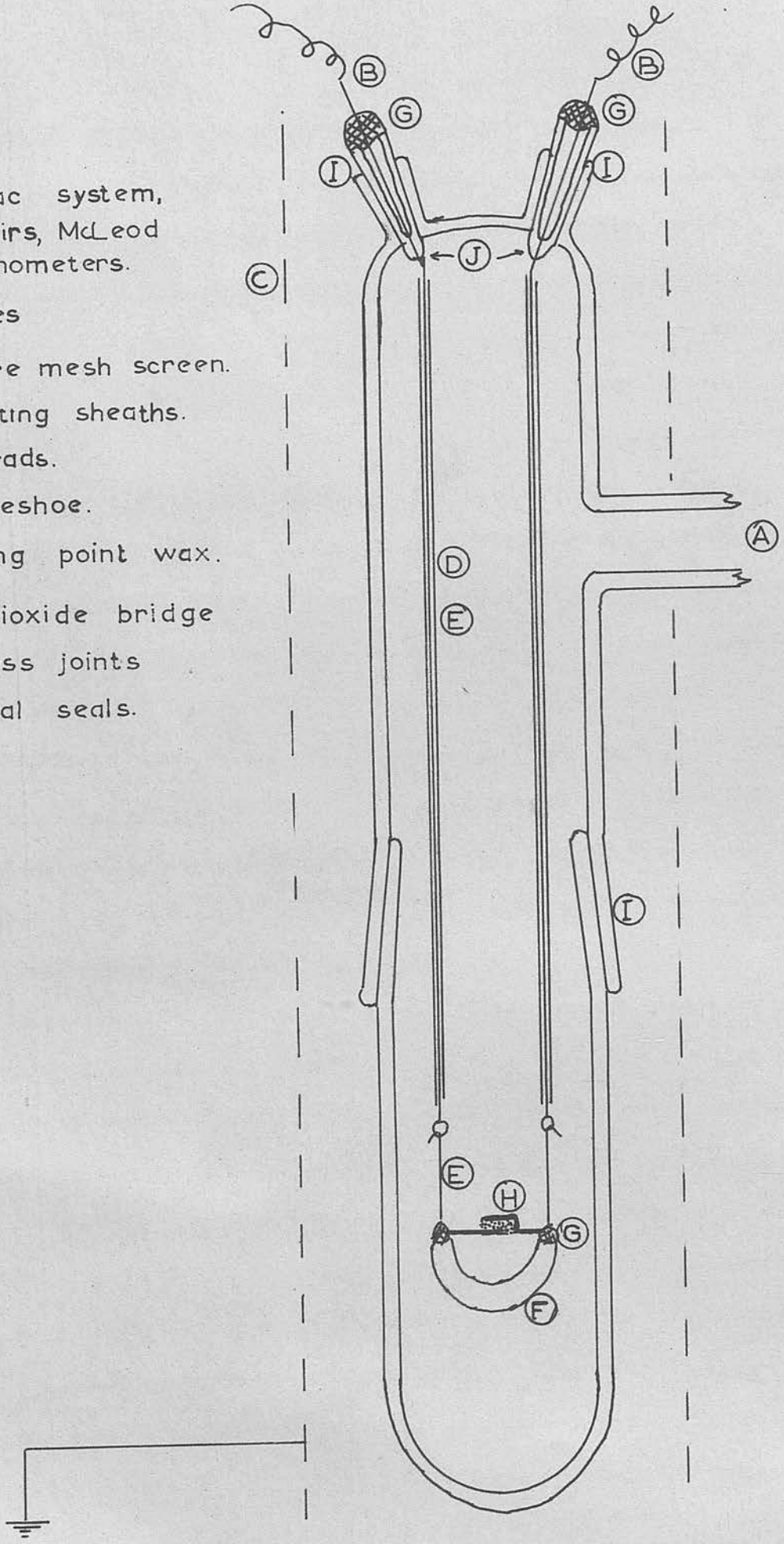
filled with dry air (Fig. 1).

(c) Thermostating. A large bath of 50 litres capacity was continually agitated with an electric stirrer. The temperature was maintained at 25°C ± .02°C by relaying a large chloroform-mercury switch through a Sunvic Control to a 500 Watt heating coil. Water was pumped from the bath by a Stuart-Turner water pump (No. 10), 5 feet vertically to a constant head where a divided flow returned to the thermostat via the Bourdon guage jacket and the reaction site (Fig. 1).

(d) A steady source of light was obtained from an Osira Mercury vapour lamp (125 Watts) operated from the mains voltage supply via a voltage stabilising control. Infra-red and ultra-violet light were filtered out after passing through a copper sulphate filter (100 gms. $CuSO_4.5H_2O$/litre) in a spherical one litre flask, and the glass of the apparatus. The flask also acted as a condenser lens. At the back of the reaction vessel a barrier type photocell gave a measure of the steadiness of the illumination. The residual light which filtered through during a run was sufficient to produce a photo current of 10 to 40 μ Amps. (Fig. 1).

(e) Bourdon Guage System. The lead to the inside of the spoon was connected to the reaction vessel while the enclosing jacket was connected to a monometer and a two way tap for adjusting the pressure. Changes in pressure across the diaphragm of the spoon caused the centre arm to deflect up or down according to whether the pressure in the reaction vessel increased or decreased. Such changes in pressure were observed through a telescope where the end of the pointer was focussed on to a scale subdivided into 100 divisions. The guage was calibrated by withdrawing air from the reaction vessel side and restoring the arm to its original position by removing air from the jacket. The total divisions traversed in any one direction across the scale is equal to the pressure/

Fig 3



Ⓐ Lead to vac system, gas reservoirs, McLeod gauge & manometers.

Ⓑ Coaxial cables

Ⓒ Earthed wire mesh screen.

Ⓓ Silica insulating sheaths.

Ⓔ Platinum leads.

Ⓕ Silica Horseshoe.

Ⓖ High melting point wax.

Ⓗ Titanium Dioxide bridge

Ⓘ Ground glass joints

Ⓙ Glass–metal seals.

pressure change on the mercury manometer connected to the guage jacket. At 74 mm. to 59 mm. pressure, a pressure change of Δp = 672 divs. was equivalent to 15.5 mm.Hg.

One scale division is then equal to 0.0230 mm. Between 59 mm. and 37 mm. one scale division was equivalent to 0.0229 mm. Throughout, the sensitivity was taken as 0.0230 mm./div. Readings were recorded to the nearest tenth of a scale division.

(f) 2-litre soda glass bulbs were used to store the various gases required during experiments. Provision was made to enable the gases to enter the reaction vessel, the subsidiary pre-treating system and the conductivity cell. A connection to a mercury manometer was also included for pressure measurements. (Fig. 1).

(g) Two cold traps were situated below the reaction vessel in such a way that any products from the titanium dioxide films could be collected in two fractions (Fig. 1).

(h) Desorbed gaseous products were analysed in a subsidiary Bourdon guage system. It consisted of an entry (ground glass joint), a cold side arm and a Bourdon guage all connected to the high vac. line (Fig. 2).

(i) Conductivity Measurements. The conductivity cell was connected to the gas reservoirs and a mercury manometer via a cold trap and also to the high vac. line and a McLeod guage. The resistance of titanium dioxide in the form of a bridge between two platinum wires 1 mm. apart was measured on a Vibron Electrometer (Electronic Industries Limited - Surrey). The bridge could be illuminated similarly to the films.

Readings were recorded at atmospheric temperature. No exact provision was made for maintaining constant temperature of the cell.

Instructions on operating the Vibron Electrometer were supplied by the makers. Best results were achieved by having all outside metal components earthed /

earthed and enclosing the cell in a wire mesh screen which was also earthed (Fig. 3).

CHEMICALS (REACTANTS)

Preparation of gases and reagents

Oxygen:- B.O.C. cylinder. Before storage the gas was dried and condensible impurities removed by passing through a cold trap at liquid oxygen temperatures.

Hydrogen:- B.O.C. cylinder as above.

Nitric Oxide:- was prepared by the method of Durham and Steacie (26). 17 gms. of sodium nitrite and 40 gms. of potassium iodide were dissolved in 100 ml. distilled water. The solution was placed in a conical flask, fitted with a dropping funnel and an outlet. Hydrochloric acid (50 ml. conc + 50 ml. distilled water) was allowed to drip into the flask from the dropping funnel. The nitric oxide produced from the reaction:-

$$2NO_2^- + 4H^+ + 2I^- \longrightarrow 2NO + I_2 + H_2O$$

was passed successively through conc H_2SO_4 and 50% KOH and was absorbed in a solution of 100 gms. $FeSO_4$ in 2 litres of slightly acid (H_2SO_4) solution. The nitric oxide was regenerated by warming the ferrous solution and separated from water vapour by passing through phosphoric oxide before being condensed in a cold trap. Nitrous oxide and other impurities were removed by fractional distillation at low temperatures. When analysed the final amount of condensible impurities amounted to about 0.01%.

Ammonia:- was prepared by the dry distillation of a mixture of calcium oxide and ammonium chloride.

$$CaO + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + H_2O$$

Some /

Some of the water and traces of carbon dioxide were removed by passing through a column of soda lime. Residual impurities (mostly water) were removed by fractional distillation between two traps at -80°C. Only the middle fractions were retained. Final purification was effected by distillation into the 2-litre storage bulb from a side arm containing KOH previously degassed at 80°C. No impurities could be detected (estimated purity 99.5 - 100.0%).

Acetone:- Hopkins and Williams, Analar Grade not less than 95% pure with a water content of 1%.

Methyl Ethyl Ketone:- May and Baker; not less than 98% pure.

Griess Llesvay Reagent (27):- for estimation of nitrites.

Solution (a) 0.1 gms. -naphthylamine dissolved in 10 ml. glacial acetic acid and 40 ml. distilled water at 40°C.

Solution (b) 0.5 gms. sulphanilic acid dissolved in the same quantities of acetic acid and water at 40°C.

Solutions (a) and (b) were mixed, made up to 250 mls. and stored in a glass stoppered flask in the dark.

Titanium dioxide Samples:- Weiser and Milligan (28).

Sample I. Thirty grams of freshly distilled titanium tetrachloride, (b.p. 135°C ± 0.5°C), were added slowly to 500 mls. distilled water. The resulting suspension of titania gel was refluxed for 6 hours and then allowed to stand until cool. After decanting the supernatant liquid the residual liberated HCl was neutralised with 2N.NaOH and refluxed for a further 6 hours. The titania gel so formed was in a very fine state of division and on removing Na^+ and Cl^- ions by washing with distilled water became colloidal in nature and increasingly difficult to throw down in the centrifuge. The residue, after washing, was dried in an air over at 160-170°C for 12 hours and then at 100°C over P_2O_5 in a pistol drier for 30 hours. The final product was a cream coloured powder and was stored in a glass stoppered bottle in the dark.

Sample/

Sample II. Thirty grams of freshly distilled titanium tetrachloride were added slowly to a 2.7 molar NaCl solution (500 mls.) and the mixture refluxed for 2 hours. The liberated HCl was neutralised with solid NaOH. At this point the supernatant liquid was decanted off and washing and drying were carried out as for Sample I.

According to Weiser and Milligan (28), Sample I and Sample II should be rutile and anatase respectively.

TECHNIQUES

Titanium dioxide films

A known quantity of titanium dioxide (0.01 - 0.10 gms.) was accurately weighed out into a clean dry reaction flask. Approximately 0.5 mls. of water (or, when stated, acetone or methyl ethyl ketone) were then added and a slurry formed. The slurry was spread out on one half of the inside of the reaction vessel so that when mounted on the reaction site it could all be illuminated. Suction from a filter pump caused the film to dry out on warming the outside of the vessel with warm water. When the film appeared to have dried out, the reaction vessel was attached via a greased ground glass joint to the subsidiary evacuating and pre-treating system and thoroughly evacuated at room temperature ($20^{\circ}C$) and 10^{-5} mm. Hg. for periods exceeding 4 days. This method gave a fairly evenly deposited film which adhered very well to the inside face.

During evacuation it was noted that water vapour was being desorbed continually, even after 3 months evacuation. It was therefore found necessary to make corrections for water produced in this way when measuring the amount recovered from evacuating an illuminated film where some photochemical reaction had occurred. The allowance was always made on the assumption, borne out by control experiments, that the water desorbed during three consecutive evacuations of equal time were in geometrical progression. The geometric mean of the amount of water obtained during a preliminary evacuation and an additional evacuation after removal of the products (all of the same duration and high vac line pressure) would be the allowance which must be subtracted from the total water obtained on removing the products. In most cases only an approximate allowance can be made for reasons which will become apparent later. Such corrections were normally small.

Uptake /

Uptake of Gases - Rate Measurements.

Pressure decrease due to the uptake of gases were followed on the Bourdon guage and noted as a function of time. The initial position of the guage pointer at the onset of a pressure change is taken as the reference value. Pressure changes were found to start in most cases at the instant of illumination though sometimes at the instant of contact between the gas phase and the film. Throughout this work the symbol Δp refers to the extent of the pressure change (in scale divisions) from the initial position and t (in minutes) refers to the time taken for a pressure change Δp to occur, either from the instant of illumination or from the instant of contact. The rate of uptake of gas, $\frac{d\Delta p}{dt}$, was measured from a smooth curve drawn through plots of Δp against t where equal Δp intervals were divided by the time taken. The mean value of the Δp interval was taken when Δp was required a a function of $\frac{d\Delta p}{dt}$. The use of the differential $\frac{dp}{dt}$ has been reserved for the case when the rate of change of pressure if given in mm./min.

$$\frac{dp}{dt} = 0.023 \frac{d\Delta p}{dt}$$

Method of Analysing Products

Normally the amounts of products obtained were either small ($\sim 20\,\mu$ moles) or large (40-150 μ moles).

Analysis of small amounts.

(a) Products obtained on desorption by evacuation.

The products were transferred to a separate part of the apparatus with a side arm and a calibrated Bourdon guage, all of known volume. Removal of the liquid oxygen surrounding the side arm was followed by a gradual evaporation of the products. The vapour pressure of the products were recorded as a function of time. The plot gave a series of steps with a step for each component. Repetition gave satisfactorily reproducible results. Any unidentified products

were/

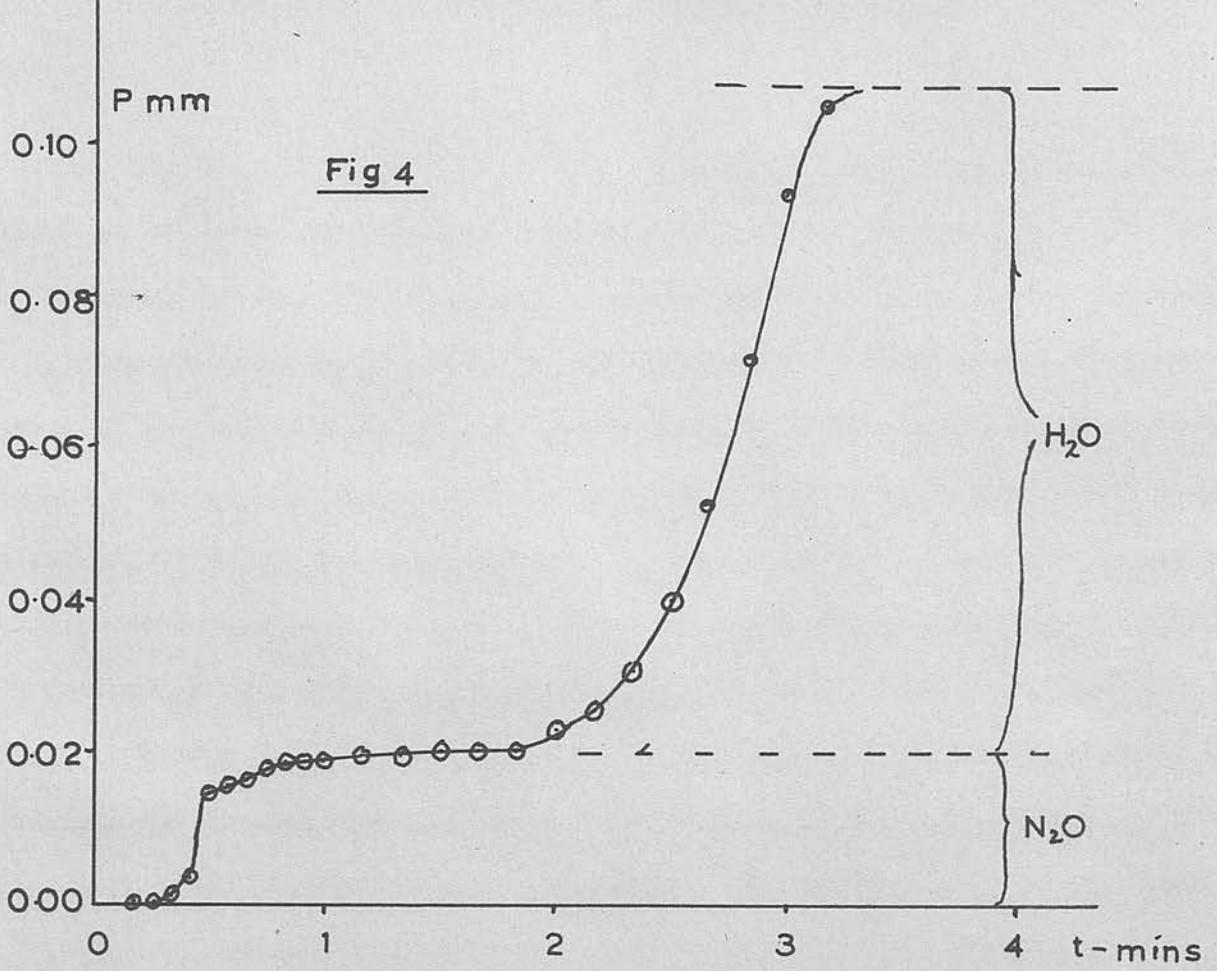

P mm
0·10
0·08
0·06
0·04
0·02
0·00
0
1
2
3
4
t-mins
H_2O
N_2O

Fig 4

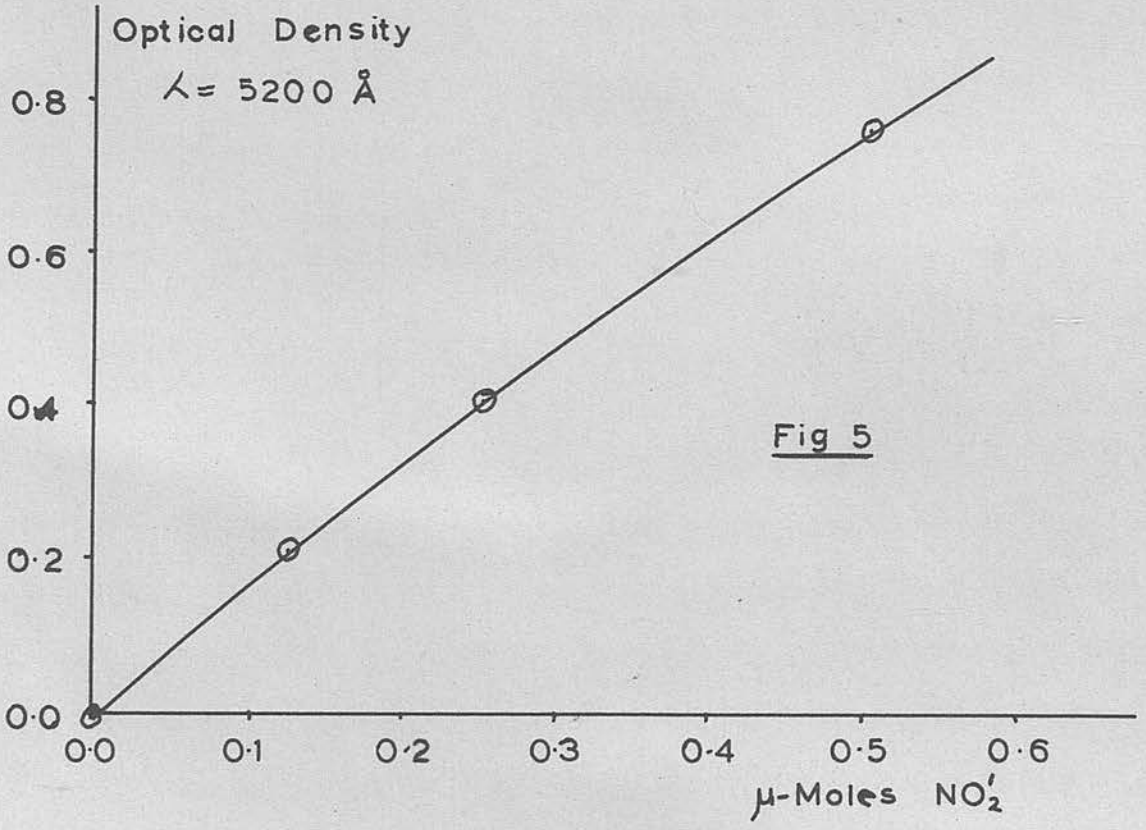

Optical Density
λ = 5200 Å
0·8
0·6
0·4
0·2
0·0
0·0
0·1
0·2
0·3
0·4
0·5
0·6
μ-Moles NO_2'

Fig 5

were isolated and analysed separately by infra-red or comparison measurements with known substances. Fig. 4 gives a typical analysis of a mixture of N_2O and H_2O by this method. For less volatile substances, particularly water, the amounts obtained by this method would tend to be low due to adsorption on the walls of the apparatus, but since the final measured pressures were low (0.03 - 0.15 mm.) with regard to saturation vapour pressures (17.5 mm. for water at 20°C) correction has not been found to be necessary. The efficiency with which water was desorbed from the films has been found liable to much greater discrepancies than that due to adsorption on measurement by this method.

(b) Non-volatile products adsorbed on the surface of films.

Throughout this work the only adsorbed products which had been identified and estimated has been nitrite. Attempts to isolate and analyse other products will be mentioned as they occur.

Estimation of small amounts of Nitrite.

The adsorbed nitrite was found to be easily extracted from the illuminated titanium dioxide films with distilled water. It was not necessary to use alkali. The aqueous extract was then made up to 100 mls. and from this an aliquot portion (5.0 mls.) was taken and made up to 20.0 mls. in a test tube with distilled water. 2.0 mls. of the Griess Llesvay reagent was added. The solution, together,with a blank of 20.0 mls. distilled water and 2.0 mls. reagent, was immersed in a bath of water at 80°C and allowed to "develop" for 10 minutes. Interaction between the nitrite and the reagent produced a pink azo dye. The optical density of the colouration was measured in a Unicam S.P. 600 and from calibration data was directly convertible to micro moles of nitrite present in the aliquot portion taken from the extract.

Calibration data for nitrite estimation:-

Solution /

Solution - 20 mls. nitrite solution + 2.0 mls. reagent.

Table III

Total Nitrite (NO_2^-) in 22.0 mls (μ)	Optical density (λ = 5200Å)
0.000	- 0.001
0.126	0.213
0.252	0.406
0.504	0.76

(See Fig 5)

For example, if 5.0 mls. of the 100 mls. extracted from a film were treated in the described manner and gave an optical density of 0.500, the amount of nitrite in the 100 mls. extract is then:-

$$\frac{100}{5.0} \times {}^{0.316} = 6.32\,\mu \text{ moles } NO_2^-$$

Analysis of large amounts of products

This problem has only arisen in connection with water ammonia mixtures. The simple method already described was unsuitable since the components interacted with one another and did not give reproducible pressure-time plots. While ammonia itself might have been separately estimated in other ways an elaboration of the simple method was developed to give accurate estimates of ammonia and water in a mixture of the two. The basic essentials were:-

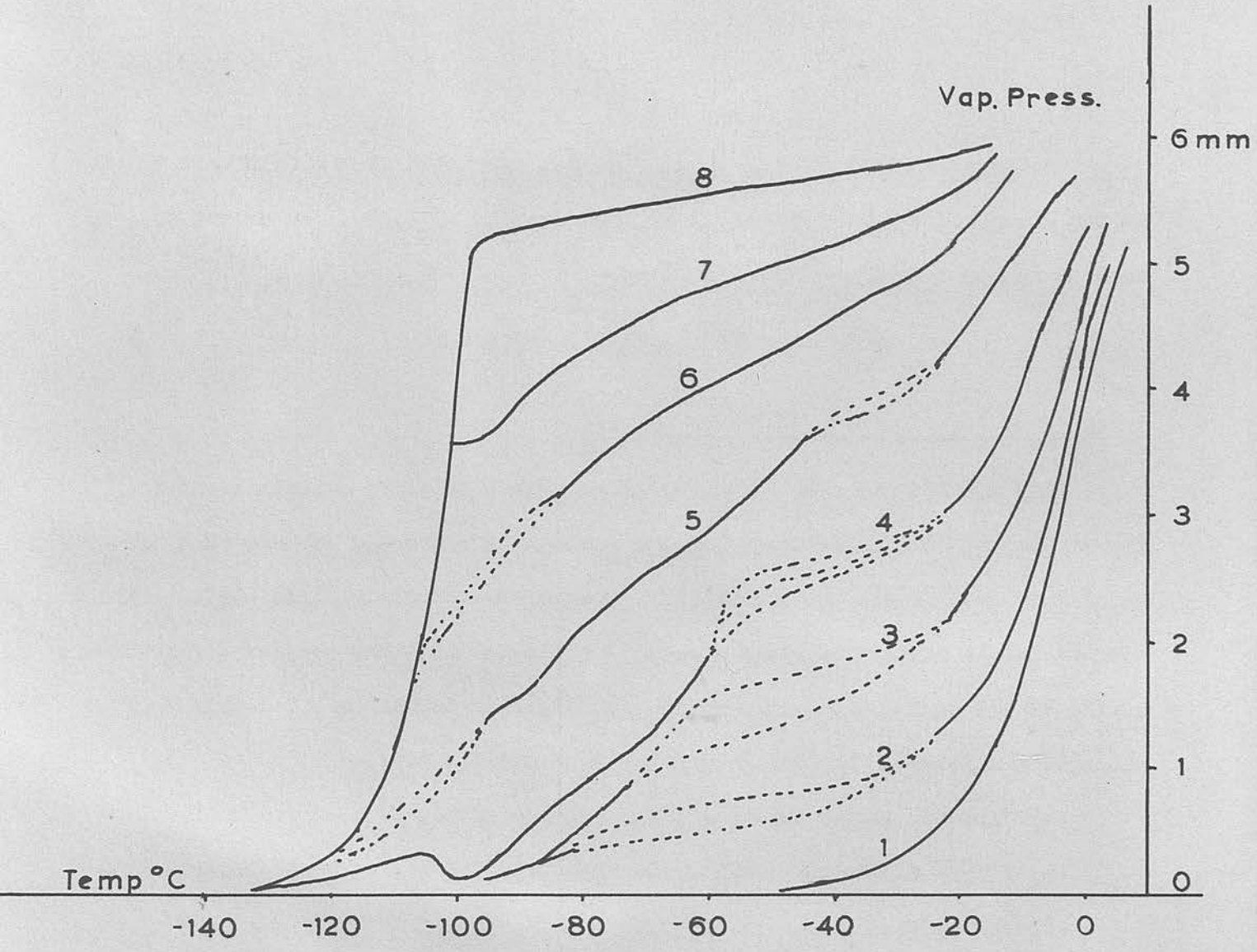
(a) Variable temperature control, -135 to +20°C.

(b) Combined ammonia-water vapour pressure of 6 mm. at room temperature.

(c) Calibration data.

The calibration data was obtained by making up a series of water-ammonia mixtures with a total combined vapour pressure of 6 mm. at 20°C, each component being measured out. The analysis vessel was fitted with a side arm and a calibrated Bourdon guage. Ammonia and water were condensed in the side arm by cooling /

Fig 6



by cooling to -186°C with liquid oxygen. Temperature control of the side arm was regulated by a cold bath of petroleum ether (b.p. fraction 40°C), contained in a Dewar vessel. -135°C could be attained by pouring liquid oxygen (or nitrogen) into a hard glass test tube suspended from the mouth of the Dewar in the ether. Temperatures between -135°C and room temperature were attained by blowing dry air through a tubualr copper coil immersed in the ether. The copper coil also acted as a stirrer. For heating the bath above -40°C it was found to be more convenient to pre-heat the dry air before passing it through the copper coil. This was simply done by passage through a glass coil immersed in hot water. By stopping the flow of air, steady temperatures could be maintained for a period of 10 minutes or longer depending upon the insulating qualities of the Dewar vessel. 10 minutes were usually sufficient to enable the water-ammonia mixtures to come to equilibrium and give a steady vapour pressure. Vapour pressure data for eight known mixtures were obtained in this manner and it was found that only certain temperature ranges gave reproducible results (Fig. 6). For high water concentrations the reproducibility ranged between -20°C and 0°C, and for relatively high ammonia concentrations between -85°C and -65°C. From Fig. 6 the vapour pressure of the mixture at -80°C, -70°C, -18°C, -12°C and -6°C were plotted against the amount of ammonia (at 20°C), initially measured out, in the form of isotherms (Fig. 7). Therefore in any mixture of water and ammonia that gave a combined pressure of 6 mm. at 20°C the amount of ammonia could be found by interpolation from the appropriate isotherms. The amount of water in the mixture could only be found approximately since a small addition had to be made to the combined pressure at 20°C to compensate for interaction and sorption on the walls of the apparatus. Fig. 8 gives an approximate estimate of the pressure corrections to be added to the mixture in order to find the water content by subtraction.

Table IV /

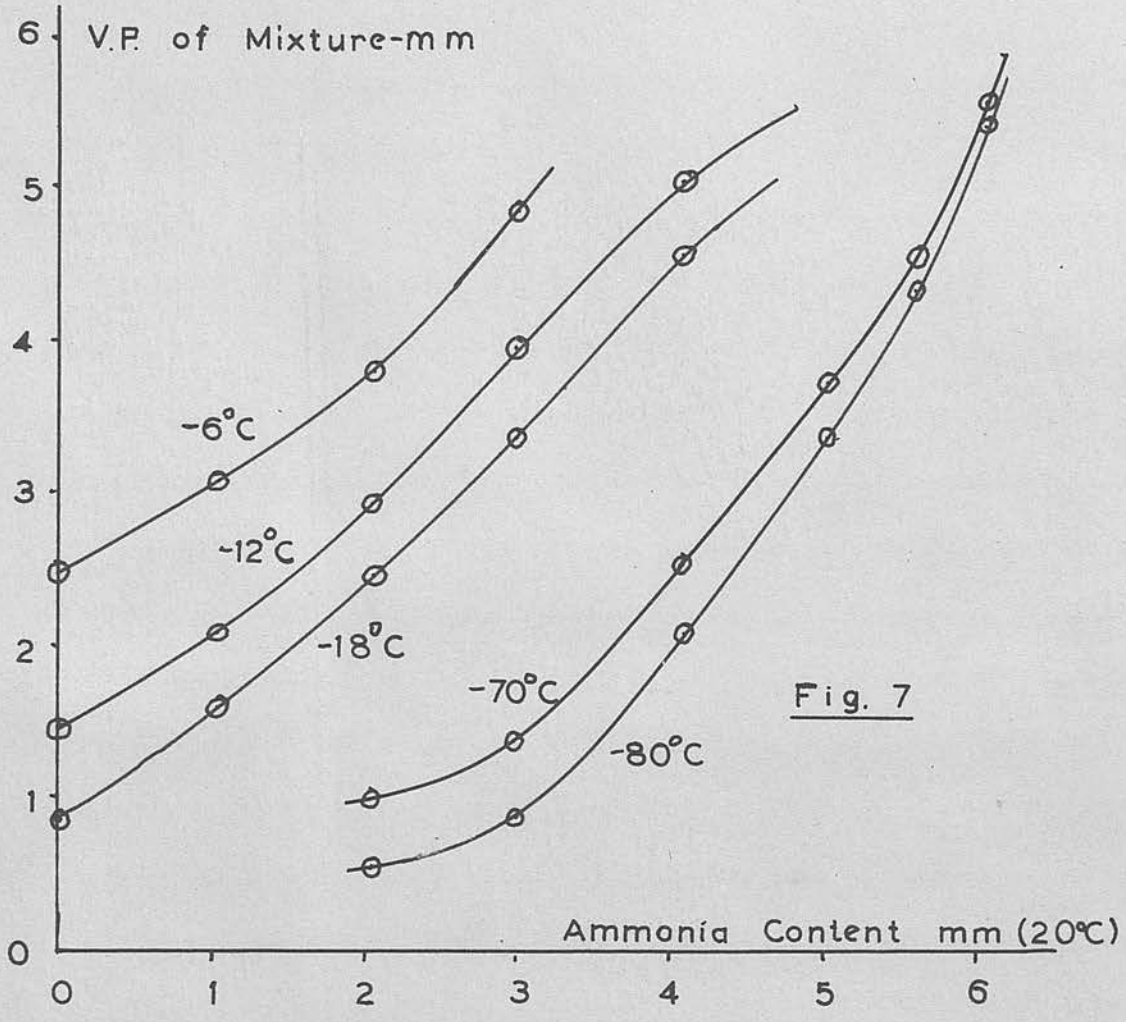

V.P. of Mixture-mm
6
5
4
3
2
1
0
-6°C
-12°C
-18°C
-70°C
-80°C
Ammonia Content mm (20°C)
0
1
2
3
4
5
6

Fig. 7

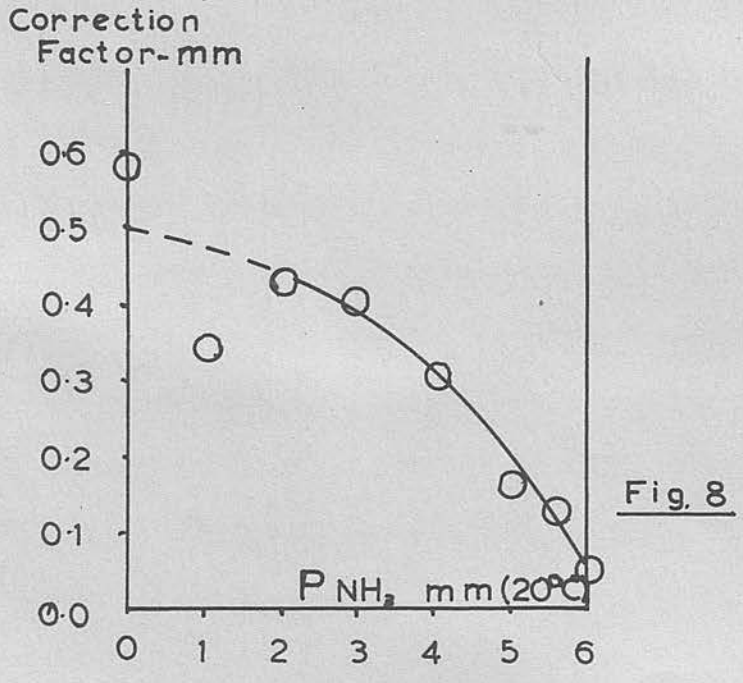

Correction Factor-mm
0·6
0·5
0·4
0·3
0·2
0·1
0·0
P NH₃ mm (20°C)
0
1
2
3
4
5
6

Fig. 8

Table IV.

	Initial Measured Pressures		Calculated $NH_3 + H_2O$	Vapour Pressure of the Mixture at					V.P. of Mixture 20°C	Correction ADD
	NH_3	H_2O		-80°C	-70°C	-18°C	-12°C	- 6°C		
(1)	0.000	6.05	6.05	-	-	0.85	1.47	2.47	5.53	0158
(2)	1.03	5.15	6.18	-	-	1.59	2.10	3.10	5.84	0.34
(3)	2.04	4.04	6.08	0.55	1.00	2.45	2.94	3.80	5.65	0.43
(4)	2.98	3.12	6.10	0.87	1.34	3.36	3.95	4.84	5.70	0.40
(5)	4.07	2.00	6.07	2.10	2.55	4.56	5.05	-	5.77	0.30
(6)	5.02	1.16	6.18	3.37	3.74	-	-	-	6.02	0.16
(7)	5.60	0.55	6.15	4.33	4.57	-	-	-	6.03	0.13
(8)	6.05	0.00	6.05	5.43	5.57	-	-	-	6.00	0.05

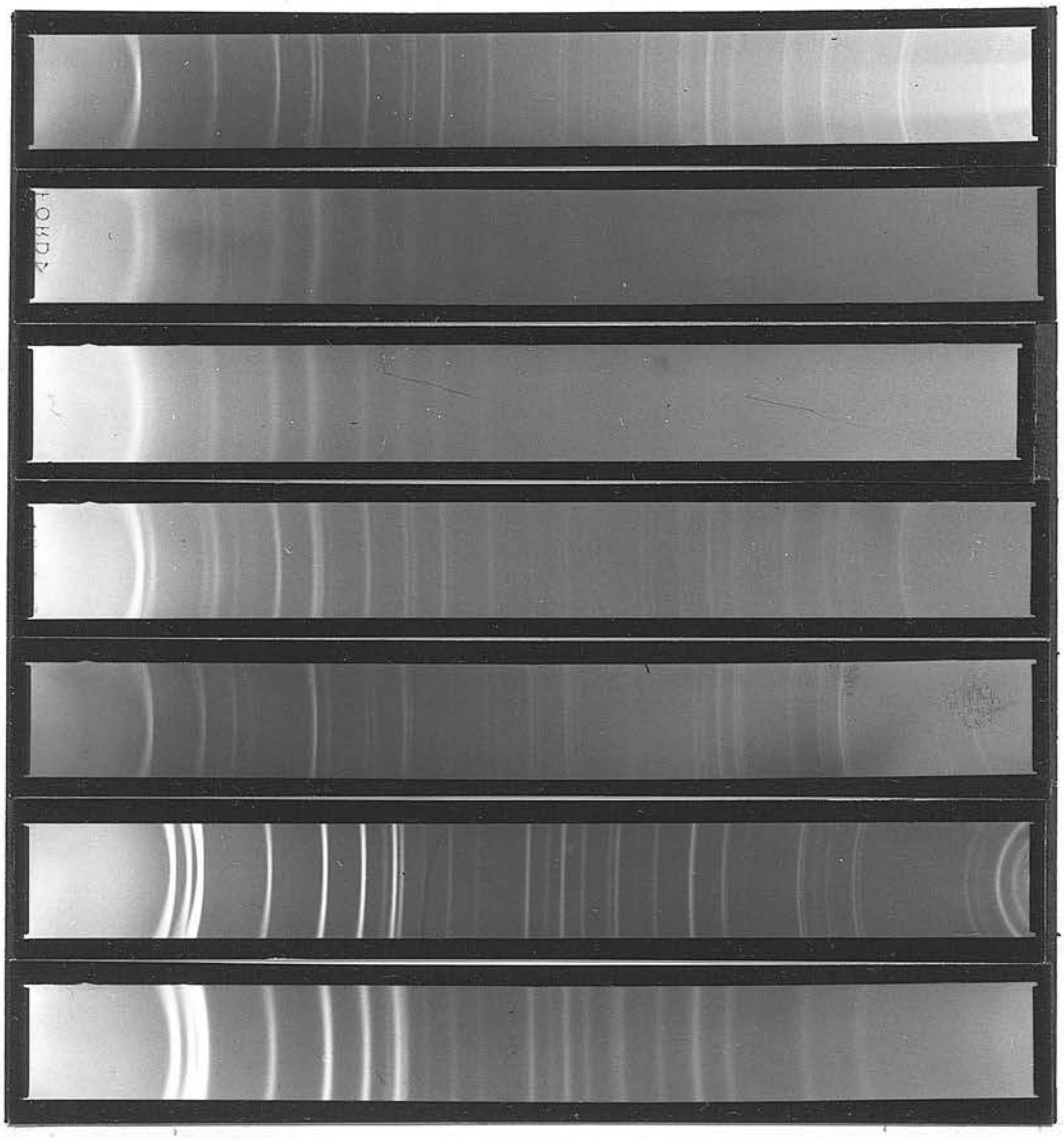
All values are quoted in mm., and are plotted in Figs. 6, 7 and 8.

Example:-

A mixture of water and ammonia gave a vapour pressure of 3.52 mm. at -80°C and 3.84 mm. at -70°C. At room temperature (20°C) the total pressure of the mixture was 6.03 mm. From the vapour pressure isotherm diagram (Fig. 7), the total ammonia in the mixture was 5.12 mm. at 20°C. The correction factor to be added to 6.03 mm. is (from Fig. 8) 0.18mm. The theoretical sum of the individual ammonia and water vapour pressures is then 6.21 mm. The analysis of the mixture is therefore 5.12 mm. NH_3 and 1.09 mm. H_2O. Quantities in micro moles could be calculated if the volume of the analysis vessel is known.

X-RAY /

Fig 9



X-RAY POWDER PHOTOGRAPHS AND PARTICLE SIZE

As has been stated, the methods of preparation of Samples I and II were such that the rutile and anatase forms were expected. Comparison of their X-ray powder photographs (Fig. 9) with those of standard rutile and anatase specimens shows that both samples were largely anatase with a small rutile content. A very small particle size is indicated by the broad and diffuse bands. Conn, Humphrey, Magee and Wallace (29) have calculated, from the broadening of the bands on an X-ray powder photograph of zinc oxide "hyperfine", that the apparent particle size is much smaller than that obtained from electron microscope measurements and this, they say, is due to the highly disordered state of the lattice. The broadening of the bands is attributed to the additional scattering effects of dislocations. In order to illustrate the possibility of a highly disordered and dislocated lattice structure in Samples I and II, X-ray powder photographs of zinc oxide (analar) and zinc oxide "hyperfine" have been included in Fig. 9 by permission of G. Walker (Edinburgh)(19). Estimated particle sizes from electron microscope examination are given in the key to Fig. 9.

Key to Fig 9.

(a) Anatase (British Titan Products Company Limited)

(b) Sample I — Particle size 40Å

(c) Sample II — " 40Å

(d) Commercial pigment; titanium dioxide prepared by vapour phase oxidation of $TiCl_4$ — " 850Å

(e) Rutile (96%) (British Titan Products Company Limited)

(f) Zinc oxide analar — Particle size 2000-3000Å

(g) Zinc oxide "hyperfine" — " 250Å

Surface/

Surface Area of Samples I and II.

An approximate estimate of the surface area can be calculated by assuming spherical particles with a mean diameter of 40Å and a density of 4.2 gms./cc.

Surface area/gm. = Number of particles/gm. X surface area/particles

i.e. $S = ns$

$$n = \frac{\text{Vol. of 1 gm.}}{\text{Vol. of 1 particle}}$$

$$= \frac{\frac{1}{\rho}}{\frac{4\pi}{3}\left(\frac{D}{2}\right)^3}$$

where ρ = density of titanium dioxide (4.2 gms./cc.)

D = mean particle diameter (40×10^{-8} cms.)

$$\text{Surface area/particle} = s = 4\pi\left(\frac{D}{2}\right)^2$$

$$\therefore \text{Surface area/gm.} = n.s = S = \frac{6}{D.\rho}$$

$$= \frac{6}{4.2 \times 40 \times 10^{-8}} \quad cm^2/gm.$$

The surface areas of Samples I and II were of the order of 350 m^2/gm.

The commercial vapour phase pigment sample had, for comparison, a surface area of approximately 17 m^2/gm.

(Voltz and Weller (30) have been able to prepare chromic oxide in a manner similar to that of Samples I and II and obtained surface areas of the order of 400 m^2/gm.).

WATER/

WATER CONTENT OF TITANIUM DIOXIDE

Literature on titania gels (14,15) gives varying water contents depending upon the method of drying. Although many observations appear to be contradictory, they are connected by two common factors, dehydration by heating and dehydration on aging. In all cases when titanium dioxide (Sample II) has been evacuated water has been found to be evolved even after months of continuous evacuation. The amounts evolved after such a time were small, 2×10^{-6} moles water from 0.1 gms. Sample II during 20 hours at 10^{-5} mm. after four weeks. Dehydration appears to be a function of time and it may be that some of the water desorbed in the latter stages was originally in the form of surface -OH groups.

$$2OH^- \longrightarrow O^{--} + H_2O$$

J. Latty (15) has shown the greatest changes in water content to occur when a hydrated gel is heated between room temperature and 300°C. Water is still evolved at 900°C.

Loss in Weight on Ignition of Sample II.

The sample was ignited in a silica crucible (ignited to constant wt.), over a bunsen to bright red heat. Cooling of the sample took place in a desiccator over phosphoric oxide at atmospheric pressure.

Wt silica crucible after ½ hour ignition	17.4468 gms.
Wt. silica crucible after 2 hours ignition (W)	17.4466 gms.
Wt silica crucible + fresh Sample II (W + w)	17.7839 gms.
Wt of Sample II (w)	0.3373 gms.

Table V

Table V

Time of ignition	W + w (gms.)	Δw%
No ignition Crucible + sample	17.7839	
1 hr.	17.7525	9.3
2 hrs.	17.7514	9.6
5 hrs.	17.7538	8.9
6 hrs.	17.7538	8.9
12 hrs.	17.7512	9.7
16 hrs.	17.7551	8.5
Treated with conc H_2SO_4 + 1 hr.	17.7547	8.6
" " " " + 2 hrs.	17.7535	9.0
" " " " + 5 hrs.	17.7540	8.9

The average loss in wt on ignition is 9.0%.

The relatively large variation in the weighings may have been due to adsorption of vapours during weighing and also, possibly, on cooling.

On the assumption that the loss in weight was due to loss of water and the final products was TiO_2, then:-

100 gms. Sample II contains 91.0 gms. TiO_2 and 9.0 gms. H_2O giving a molecular ratio of $TiO_2 : H_2O = 1.00 : 0.44$.

Lossiin Weight on evacuation of Sample II ($20^{\circ}C$)

1 gm. of Sample II was accurately weighed out into a 25 ml. r.b. flask fitted with a ground glass joint. Into this joint was fitted an adaptor and a high vac. tap. The whole apparatus was detached from a high vac. entry (K) for weighing - See Fig. 1.

Weight of r.b. flask (25 ml.) + Sample II	18.8458 gms.
Weight of r.b. flask	17.6815 gms.
Wt Sample II	1.1643 gms.
Total weight of apparatus	58.8397 gms.
Volume (internal)	32.3 mls.
Wt 32.3 mls. air at atmospheric pressure ($20^{\circ}C$)	0.0386 gms.
Theoretical wt. of evacuated apparatus (W + w)	58.8011 gms.

Table VI/

Table VI

Degree of evacuation	W + w gms.	w%
Air free apparatus	58.8011	-
2 mins. with oil pump (10^{-2} mm. Hg)	58.8008	0.05
4 hrs. at 10^{-5} mm. Hg.	58.7680	2.84
6 hrs. "	58.7655	3.06
25 hrs. "	58.7622	3.34
29 hrs. "	58.7624	3.33
2 days "	58.7609	3.45
5 days "	58.7602	3.52
10 days "	58.7581	3.69
11 days "	58.7581	3.69
14 days "	58.7587	3.64
23 days "	58.7593	3.59
24 days "	58.7593	3.59

The loss in wt (w) of the Sample on exhaustive evacuation was 3.6%, again on the assumption that the loss was due to water removed.

100 gms. Sample II $\xrightarrow{\text{(ignition)}}$ (91.0 gms. TiO_2) + 9.0 gms. H_2O.

(exhaustive evacuation) ↓

(91.0 gms. TiO_2 + 5.4 gms. H_2O) + 3.6 gms. H_2O.

The water content of the residual evacuated titanium dioxide was such that the ratio of TiO_2 : H_2O was 4.0 : 1.04. Quantitatively, 5.4 gms. H_2O in 96.4 gms. evacuated Sample II were equivalent to 3120 x 10^{-6} moles water/gm.

The covering area of a chemisorbed water molecule may be assumed to occupy 15Å^2 (= area of two OH^- ions) (31). On this basis the water not removed by evacuation had a covering area of 280 m^2/gm. if it existed entirely as OH^- groups on the surface. This would approximate to a surface monolayer of OH^- groups.

OPTICAL/

OPTICAL DENSITY OF A COLLOIDAL SUSPENSION OF SAMPLE II

0.1 gms. Sample II were shaken up with distilled water and allowed to stand in the dark for 2 hours to enable the heavier particles to settle out. Measurements of the optical density of the resulting colloidal suspension, by a Unicam S.P. 500 spectrophotometer, showed increasing values over the range 4360 - 4050 - 3650Å. Maxima occurred at 2950Å and 2430Å with the possibility of a third maximum at a shorter wavelength (Fig. 10). The absorption of light as given by the optical density of the suspension must include the loss in direct transmission due to scattering effects, the intensity of the scattered light (I_s) by the Rayleigh equation (32):-

$$I_s = \frac{24\pi^3}{\lambda^4} \cdot \frac{(m^2 - 1)^2}{(m^2 + 2)^2} \cdot V$$

is inversely proportional to λ^4 where m is the ratio of the refractive indices of particle and medium and V is the particle volume. The observed optical density values are too large in the sense that the light available for absorption by the particle has been reduced by scattering and the transmitted light is too small, and hence, if a is the scattering factor, corrected optical density values will be given by:-

$$D = \log \frac{I_o}{I_t + \frac{a}{\lambda^4}}$$

where I_o = Intensity of incident light and I_t = Intensity of the transmitted light.

Correlation between the observed uncorrected optical densities and the relative rates of oxygen uptake at varying wavelengths can be shown to exist, suggesting that the amount of light scattered was approximately the same in the optical density measurements as in the photo experiments. This, in turn, suggests that the scattered light was small in both instances, since the conditions are very different in the two sets of determinations.

Table VII/

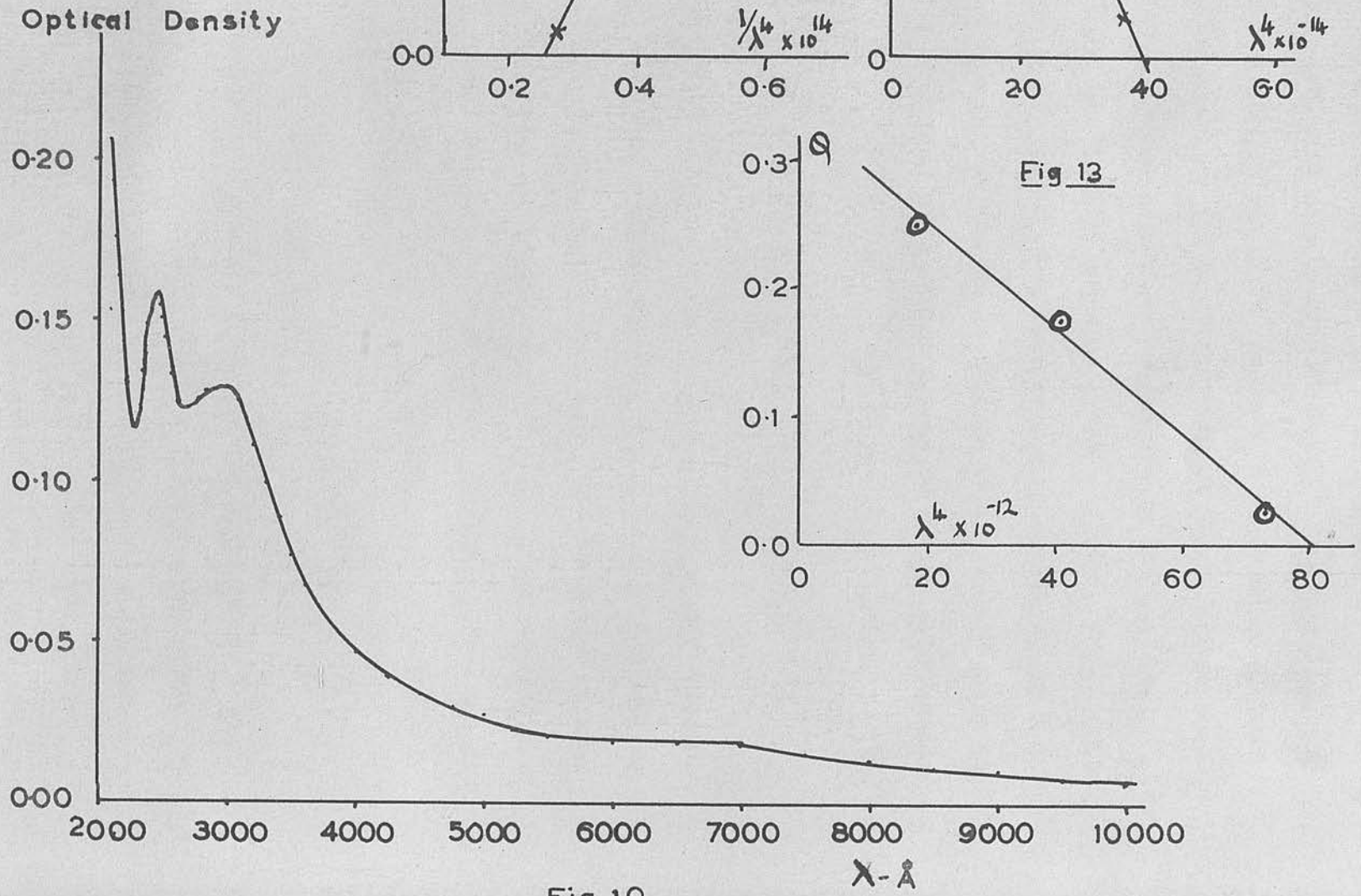


Fig 10

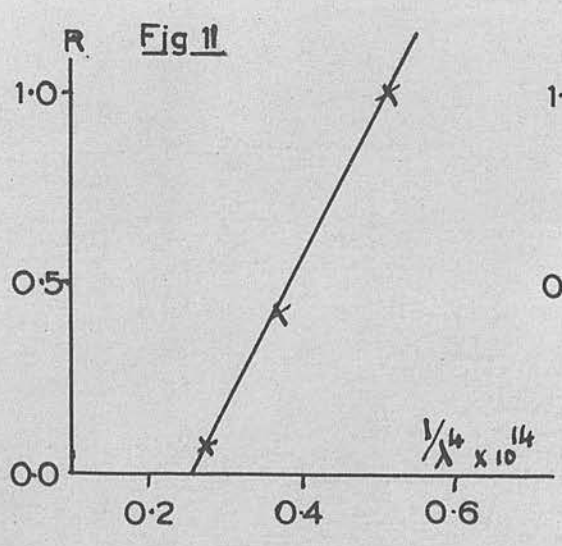


Fig 11

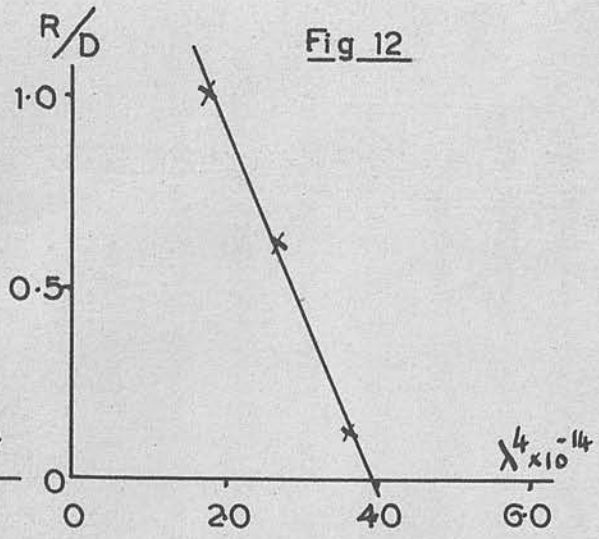


Fig 12

Fig 13

Table VII

Rel. opt. density (D)	Rel. Rate (R)	$\frac{R}{D}$	(Å)	$\lambda^4 \times 10^{-14}$	$\frac{1}{\lambda^4} \times 10^{14}$
1.00	1.00	1.00	3650	1.77	0.515
0.69	0.42	0.61	4050	2.70	0.370
0.56	0.065	0.116	4360	3.62	0.276

See Figs. 11 and 12. λ_o is the extrapolated value of λ for R and $\frac{R}{D} = 0$.

Kennedy's measurements on the relative rate of oxygen uptake were based upon unit intensity of incident light at λ = 3650, 4050 and 4360Å.

The relative rate (R) was found to be a function of $1/\lambda^4$:-

$$R = 3.26 \left(\frac{1}{\lambda^4} - \frac{1}{\lambda_o^4}\right) \times 10^{14} \qquad (1) \quad \text{(Fig. 11)}$$

and the function $\frac{R}{D}$ was found to be dependant upon λ^4:-

$$\frac{R}{D} = \frac{1}{2.17} \left(\lambda_o^4 - \lambda^4\right) \times 10^{-14} \qquad (2) \quad \text{(Fig. 12)}$$

eliminating R from 1 and 2:-

$$D = \frac{2.17.R}{(\lambda^4 - \lambda_o^4) \times 10^{-14}}$$

$$D = \frac{7.06 \left(\frac{1}{\lambda^4} - \frac{1}{\lambda_o^4}\right)}{(\lambda_o^4 - \lambda^4)} \times 10^{28} \qquad (3)$$

where λ_o (= 4410Å) (from Figs. 11 and 12), is the threshhold wavelength of light capable of causing a photosorption of oxygen.

In the photo reaction:- $KNO_3 \xrightarrow{h\nu} KNO_2 + O$ (Gillam and Morton (33)), the quantum efficiency (Q) is found to be a linear function of λ^4:-

Quantum /

Quantum efficiency (Q)	λ Å	$\lambda^4 \times 10^{-12}$
0.25	2070	18.4
0.17	2550	41
0.024	2820	73

in the same way as the value $\frac{R}{D}$ for the uptake of oxygen is a linear of λ^4 (Fig. 13). In the case of KNO_3 the threshhold wavelength for photochemical reactions is $\lambda_o = 3000$Å (see Fig. 13), i.e. Q = 0 when $\lambda = 3000$Å

$$Q = \frac{1}{2.40} (\lambda_o^4 - \lambda^4) \times 10^{-12} \qquad (4)$$

The similarity between equations 2 and 4 indicates that

$$\frac{R}{D} = K.Q \qquad (5)$$

i.e. that the rate of uptake of oxygen (R) is directly proportional to the Quantum efficiency (Q) and the optical density of the titanium dioxide (D). All three quantities depend upon the wavelengths of incident light - see equations 1, 3 and 4.

It is noted in passing that the light absorption of a solution of potassium nitrate commences at 3300Å rises to a maximum at 3000Å. The photo reaction:-

$$KNO_3 \longrightarrow KNO_2 + O$$

does not occur at $\lambda >$ 3000Å. On a parallel basis the light absorption characteristics of aqueous suspensions of titanium dioxide is not, in itself, characteristic of photo-degradative properties.

PHOTO-/

PHOTO-UPTAKE OF OXYGEN ON TITANIUM DIOXIDE

During studies in the uptake of oxygen on acetone bound films of titanium dioxide it soon became apparent that complicating factors were being incurred. The oxygen uptake was attended by the production of water and also carbon dioxide, the latter causing complications in the determination of the theoretical limit of the oxygen uptake. It was only possible, after obtaining results for water bound films, to interpret the data collected. To preserve continuity, the photo-uptake of oxygen on water bound films will be dealt with first.

PHOTO-UPTAKE OF OXYGEN ON WATER BOUND FILMS

Film 1.

Wt. Sample II	0.0816 gms.	(wt. after evacuation)
Reaction volume	33.9 mls.	
Oxygen pressure	50.1 mm.	

(For experimental procedure see text pp. 26)

The twenty-four hours evacuation immediately preceding the admission of oxygen to the film, yielded 6.4 μ moles of water vapour. A twenty-four hour evacuation immediately following the illumination produced 10.4 μ moles of water vapour. A third twenty-four hour evacuation immediately following the second yielded 2.9 μ moles H_2O. Subtraction of the geometric mean of the first and third water desorptions (4.3 μ) from that desorbed during the second gave 6.1 μ moles H_2O (ΔH_2O), as a measure of that produced photochemically in presence of oxygen. The oxygen pressure decrease observed on illumination was equivalent to 3.32 μ moles. (Small quantities of water vapour (10-20 μ) could be adsorbed on the surface of the film to give a negligible vapour pressure with respect to the observed pressure decrease). It is clear from this that one oxygen molecule could have been responsible for the release of two water molecules.

$$\Delta O_2 : \Delta H_2O = 3.32 : 6.1 = 1.00 : 1.84$$

No evidence of any carbon dioxide was found. Such a ratio, admittedly, can only be regarded as approximate in that the correction for thermally released water vapour (before and after illumination) is relatively large. Repetition showed, however, that the effect was undoubtedly genuine; the water found immediately after illumination was always greater than that released by preliminary or final evacuation - see subsequent films.

Characteristics and Extent of Oxygen Uptake

Film 2.

Wt. Sample II	0.0735 gms.	(wt. after evacuation)
Reaction volume	28.6 mls.	
Initial oxygen pressure	50.3 mm.	
Guage sensitivity	0.0230 mm./div.	

The usual preliminary evacuation produced 4.15 μ H_2O, ($\Delta_1 H_2O$), and after admitting oxygen, illumination caused a pressure decrease. The time t (mins.) taken to attain a pressure change of Δ p divs. is given below.

Table VIII/

Table VIII

t mins.	Δp divs.	t	Δp	t	Δp	t	Δp
0	0.0	26	9.9	455	61.0	4805	181.9
½	0.1	29	10.9	471	62.2	5880	196.0
1	0.7	35	12.3	482	63.1	5992	197.3
2	1.2	40	13.8	1402	112.6	6120	197.9
3	1.8	48	15.7	1506	116.7	6195	198.0
4	2.1	55	17.0	1598	119.3	6295	198.8
5	2.8	60	18.1	1684	121.7	6508	199.2
6	3.2	73	20.6	1763	123.7	6540	199.9
7	3.8	82	22.3	1849	125.8	7253	208.0
8	4.1	94	24.5	2840	149.4	7325	208.0
9	4.3	100	25.3	2943	150.9	7530	209.8
10	4.9	112	27.3	3040	152.6	7615	209.9
11	5.1	171	35.7	3171	156.6	7825	211.9
12	5.4	192	37.9	3276	157.4	7905	212.9
13	5.8	220	41.0	3333	158.8	7990	213.4
14	6.1	246	43.8	3437	160.7	8610	219.2
15	6.6	276	46.7	3495	161.7	8707	219.8
16	6.8	301	48.9	3705	165.6	8786	220.0
17	7.1	329	51.1	4290	174.5	8889	220.8
18	7.3	349	53.0	4417	175.9	8990	221.7
19	7.9	371	54.5	4500	177.3	9083	222.0
20	8.0	385	56.4	4610	179.1	light off	
222	8.7	420	58.2	4697	179.9	10050	223.8
23	9.0	439	59.7				

Derived values from Table VIII are given in Table IX (Fig. 14). A derived $\log \frac{d\Delta p}{dt}$ - Δp plot for film 1 is included in Fig. 14.

Table IX/

Fig 15

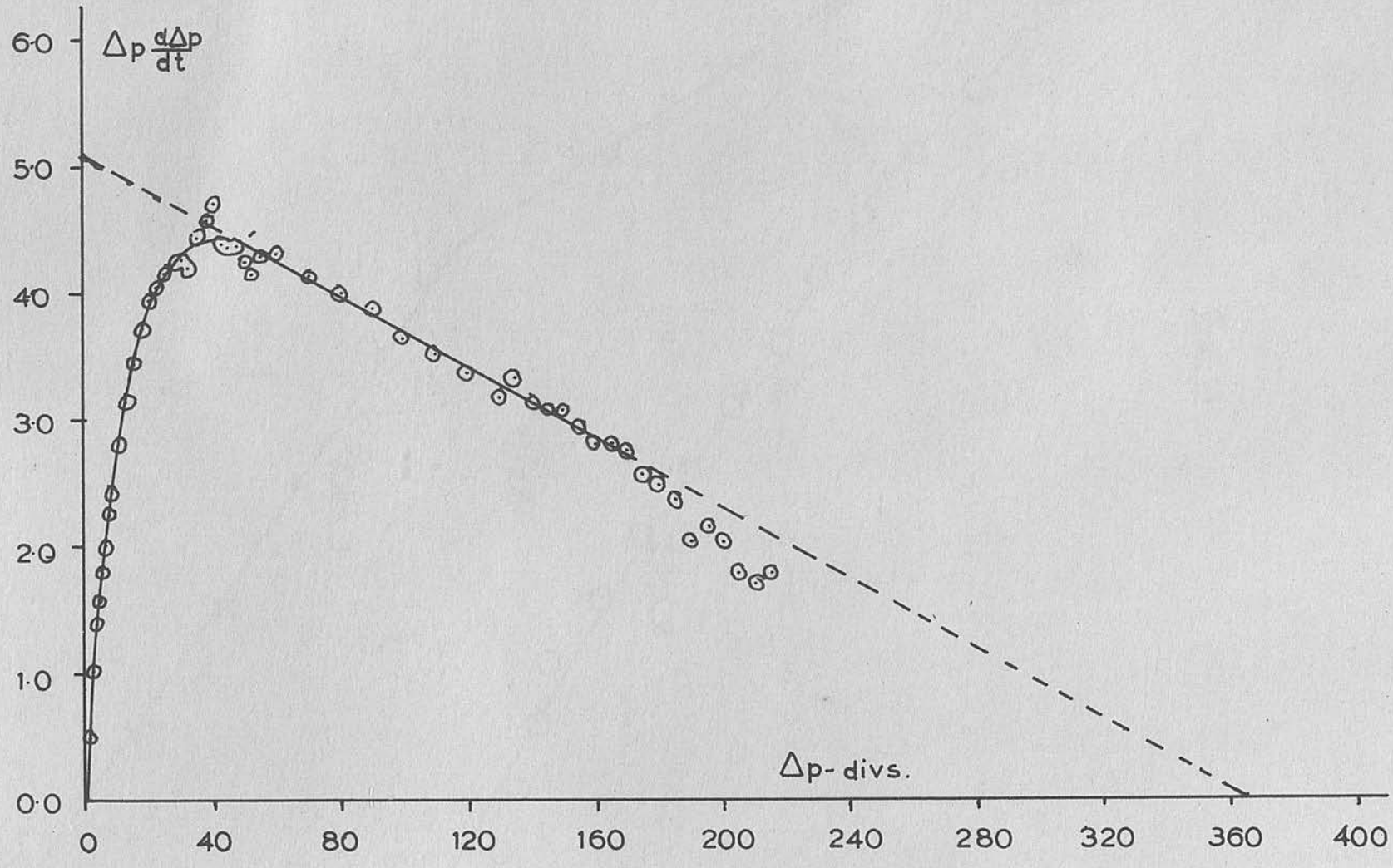

6·0
5·0
4·0
3·0
2·0
1·0
0·0
$\Delta p \frac{d\Delta p}{dt}$
Δp- divs.
0
40
80
120
160
200
240
280
320
360
400

Table IX

Δp	$\log \frac{d\Delta p}{dt}$	$\frac{d\Delta p}{dt} \cdot \Delta p$	Δp	$\frac{d\Delta p}{dt} \cdot \Delta p$
1	$\bar{1}.688$	0.488	55	4.29
2	$\bar{1}.705$	1.010	60	4.32
3	$\bar{1}.662$	1.378	70	4.13
4	$\bar{1}.591$	1.560	80	4.00
5	$\bar{1}.551$	1.780	90	3.87
6	$\bar{1}.525$	1.010	100	3.65
7	$\bar{1}.507$	2.25	110	3.52
8	$\bar{1}.491$	2.480	120	3.36
10	$\bar{1}.449$	2.81	130	3.17
12.5	$\bar{1}.401$	3.14	135	3.33
15	$\bar{1}.360$	3.43	140	3.12
17.5	$\bar{1}.326$	3.71	145	3.07
20	$\bar{1}.295$	3.74	150	3.06
22.5	$\bar{1}.255$	4.05	155	2.92
25	$\bar{1}.223$	4.17	160	2.80
27.5	$\bar{1}.185$	4.21	165	2.80
30	$\bar{1}.152$	4.26	170	2.74
32.5	$\bar{1}.111$	4.19	175	2.55
35	$\bar{1}.104$	4.44	180	2.48
37.5	$\bar{1}.086$	4.57	185	2.36
40	$\bar{1}.072$	4.72	190	2.03
42.5	$\bar{1}.013$	4.38	195	2.14
45	$\bar{2}.987$	4.37	200	2.02
47.5	$\bar{2}.964$	4.37	205	1.78
50	$\bar{2}.929$	4.25	210	1.69
52.5	$\bar{2}.898$	4.15	215	1.77

An examination of the rate of pressure decrease ($\frac{d\Delta p}{dt}$) values obtained from Table VIII showed the uptake to be divisible into two distinct parts (a) and (b).

(a) In the initial stages the oxygen uptake was found to agree with the Roginsky-Zeldovich equation for chemisorption:-

$$\frac{dq}{dt} = ae^{-bq} \quad (34, 35, 36, 37, 38),$$

where q is the amount of gas chemisorbed at time = t, a and b are constants. Since pressure changes are measured in a constant volume system q in this case can be represented by Δp.

$$\frac{d\Delta p}{dt} = ae^{-b\Delta p}$$

$$\log \frac{d\Delta p}{dt} = \log a - b\Delta p$$

by putting $\log a = b\Delta p'$

$$\log \frac{d\Delta p}{dt} = b(\Delta p' - \Delta p)$$

in Fig. 14 a plot of $\log_{10} \frac{d\Delta p}{dt}$ against Δp shows two linear portions up to $\Delta p = 15$ divs. with two separate sets of values for b and $\Delta p'$.

Film 1	Film 2
b = - 0.0780, - 0.0517	b = - 0.0591, - 0.0194
$\Delta p'$ = 4.0, 15.8	$\Delta p'$ = 4.7, 14.5

The third portion of the Roginsky-Zeldovich plot (i.e. beyond $\Delta p = 15$ divs.) is non linear.

(b) Above $\Delta p = 40$ divs. and up to $\Delta p = 170$ divs. the relation between $\frac{d\Delta p}{dt}$ and Δp is:-

$$\frac{d\Delta p}{dt} = \frac{K'}{\Delta p} + K''$$

i.e. $$\frac{d\Delta p}{dt} = K \frac{\Delta p' - \Delta p}{\Delta p}$$ (See Fig. 15)

Where $\Delta p = 365$ divs. and is the extrapolated value of Δp when $\frac{d\Delta p}{dt} = 0$ and K, the gradient, = - 0.014

$$\therefore \quad \frac{d\Delta p}{dt} = - 0.014 \left(\frac{365 - \Delta p}{\Delta p}\right)$$

This equation holds for the later stages ($40 < \Delta p < 170$). Discontinuity, beyond $\Delta p = 170$ divs., may be due to release of CO_2 from the film to the gas phase thereby reducing the observed rate of pressure decrease. Kennedy (13) has shown that the heating of laboratory prepared samples to 800°C results in the production of large quantities of CO_2 ($\sim 200 \mu/gm$), i.e. comparable to the amount/

amount of active sites.

Products.

Preliminary evacuation $\Delta_1 H_2O = 4.15\,\mu$

A twenty-four hour evacuation of the exposed film (2) produced the following:-

$$\Delta_2 H_2O = 15.4\,\mu$$

$$\Delta CO_2 = 1.5\,\mu$$

Further evacuation for twenty-four hours produced:-

$$\Delta_3 H_2O = 3.5\,\mu$$

$$\Delta CO_2 = 0.0\,\mu$$

The uptake of oxygen in this case produced a small amount of CO_2.

The calculated amount of water, $(\Delta_1 H_2O . \Delta_3 H_2O)^{\frac{1}{2}}$, produced by aging during the evacuation of film 2 after exposure was 3.8 . The amount produced photochemically was $15.4 - 3.8 = 11.6\,\mu$ (ΔH_2O).

The observed pressure decrease at the end of the illumination was 223.8 divs. Since this occurred in a volume of 28.6 mls. at 25°C and 1 div. = 0.0230 mm. the pressure decrease in micromoles was calculated on the basis that 1 gm. mole of gas occupies 22400 mls. at 0°C and 760 mm.:-

$$\Delta p = \frac{223.8 \times .023 \times 28.6 \times 273}{760 \times 22400 \times 298} \times 10^6\,\mu \text{ moles.}$$

$$= 8.2\,\mu \text{ moles.}$$

Since there was the strong possibility of some CO_2 existing in the gas phase, the value $\Delta p = 8.2$ moles is probably low and the oxygen uptake was between Δp and $\Delta p + CO_2$.

$$\text{i.e.} \quad O_2 = 9.0 \pm 0.7 \quad \text{moles.}$$

An uptake of $O_2 = 9.0 \pm 0.7$ moles has resulted in the production of

H_2O/

$\Delta H_2O = 11.6\mu$ and $\Delta CO_2 = 1.5\mu$. The amount of the oxygen in the products (7.3 μ moles O_2) was slightly lower than that photosorbed.

Extent of Oxygen Uptake

If the discontinuity of the linearity in Fig. 15 is attributed for the present, to the gaseous evolution of CO_2, starting when $\Delta p = 170$ divs., then the rate of the uptake of oxygen reached zero when $\Delta_\infty p = 365$ divs. This amount was equivalent to an uptake of:-

$$\Delta_\infty p = \Delta_\infty O_2 = 176\,\mu \text{ moles/gm.}$$

Summary of Oxygen Uptake on Water Bound Films

(a) The uptake of oxygen resulted in the production of water and small amounts of CO_2:-

$\Delta O_2 = 9.0 \pm 0.7\mu$ $\Delta H_2O = 11.6\mu$ and $\Delta CO_2 = 1.5\mu$.

(b) The extent of the oxygen uptake was 176 μ moles/gm.

(c) In the initial stages an agreement was found with the Roginsky-Zeldovich equation for chemisorption:-

$$\log \frac{d\Delta p}{dt} = b'(\Delta p' - \Delta p)$$

where b and $\Delta p'$ have apparently two sets of values (Fig. 12).

(d) In the later stages of the uptake an agreement with the equation:-

$$\frac{d\Delta O_2}{dt} = K\left(\frac{\Delta_\infty O_2 - \Delta O_2}{\Delta O_2}\right)$$

was found where in this case $\Delta p = \Delta O_2$.

PHOTO-/

PHOTO-UPTAKE OF OXYGEN IN PRESENCE OF HYDROGEN

Film 3.

Wt. Sample II	0.0552 gms. (Wt. after evacuation)
Reaction volume	59.6 mls.
Initial oxygen pressure	49.3 mm.
Initial hydrogen pressure	51.5 mm.
Guage sensitivity	0.0230 mm./div.

The decrease in pressure (Δp divs.) in illumination is given as a function of time (t mins.) in Table X.

Table X

t	Δp	t	Δp	t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	$5\frac{1}{2}$	1.8	20	5.0	238	22.95	750	39.7	3320	74.1
$\frac{1}{4}$	0.0	6	1.9	21	5.4	274	24.85	1470	53.1	4320	77.3
$\frac{1}{2}$	0.05	7	1.9	22	5.3	300	26.0	1540	54.1	4380	78.4
$\frac{3}{4}$	0.1	8	2.6	23	5.5	318	26.3	1580	54.5	4455	79.4
1	0.2	9	2.8	28	6.0	356	27.8	1730	56.2	4630	81.3
$1\frac{1}{4}$	0.1	10	2.7	36	7.2	400	29.4	1775	56.6	4720	83.0
$1\frac{1}{2}$	0.5	11	3.0	40	8.0	455	31.1	1840	57.1	4765	83.0
$1\frac{3}{4}$	0.6	12	3.4	62	10.8	580	36.2	1870	57.8	5750	86.5
2	0.6	13	3.6	73	11.9	589	36.1	2895	70.2	5820	87.2
$2\frac{1}{2}$	0.8	14	3.9	83	14.1	603	36.3	2950	70.8	5900	87.6
3	0.9	15	3.9	111	15.7	645	37.4	3010	71.0	6127	90.2
$3\frac{1}{2}$	1.05	16	4.1	121	16.1	674	37.95	3060	71.3	6170	91.0
4	1.15	17	4.2	152	18.4	696	38.8	3168	72.2	Illum. Discon.	
$4\frac{1}{2}$	1.6	18	4.2	179	19.9	705	38.6	3225	72.9	Dark uptake	
5	1.8	19	4.7	200	21.2	732	39.7	3270	73.1	10,000	94.7

Derived values from Table X are given in Tables XI and XII.

Table XI

Δp	$\log \frac{d\Delta p}{dt}$	Δp	$\log \frac{d\Delta p}{dt}$	Δp	$\log \frac{d\Delta p}{dt}$	Δp	$\log \frac{d\Delta p}{dt}$
1	$\bar{1}.543$	6	$\bar{1}.188$	12.5	$\bar{2}.996$	24.5	$\bar{2}.659$
2	$\bar{1}.427$	7	$\bar{1}.149$	14.5	$\bar{2}.924$	27.5	$\bar{2}.593$
3	$\bar{1}.352$	8	$\bar{1}.124$	17.5	$\bar{2}.833$	29.5	$\bar{2}.553$
4	$\bar{1}.297$	9	$\bar{1}.104$	19.5	$\bar{2}.777$	32.5	$\bar{2}.507$
5	$\bar{1}.233$	9.5	$\bar{1}.097$	22.5	$\bar{2}.702$	34.5	$\bar{2}.479$

Table XII/

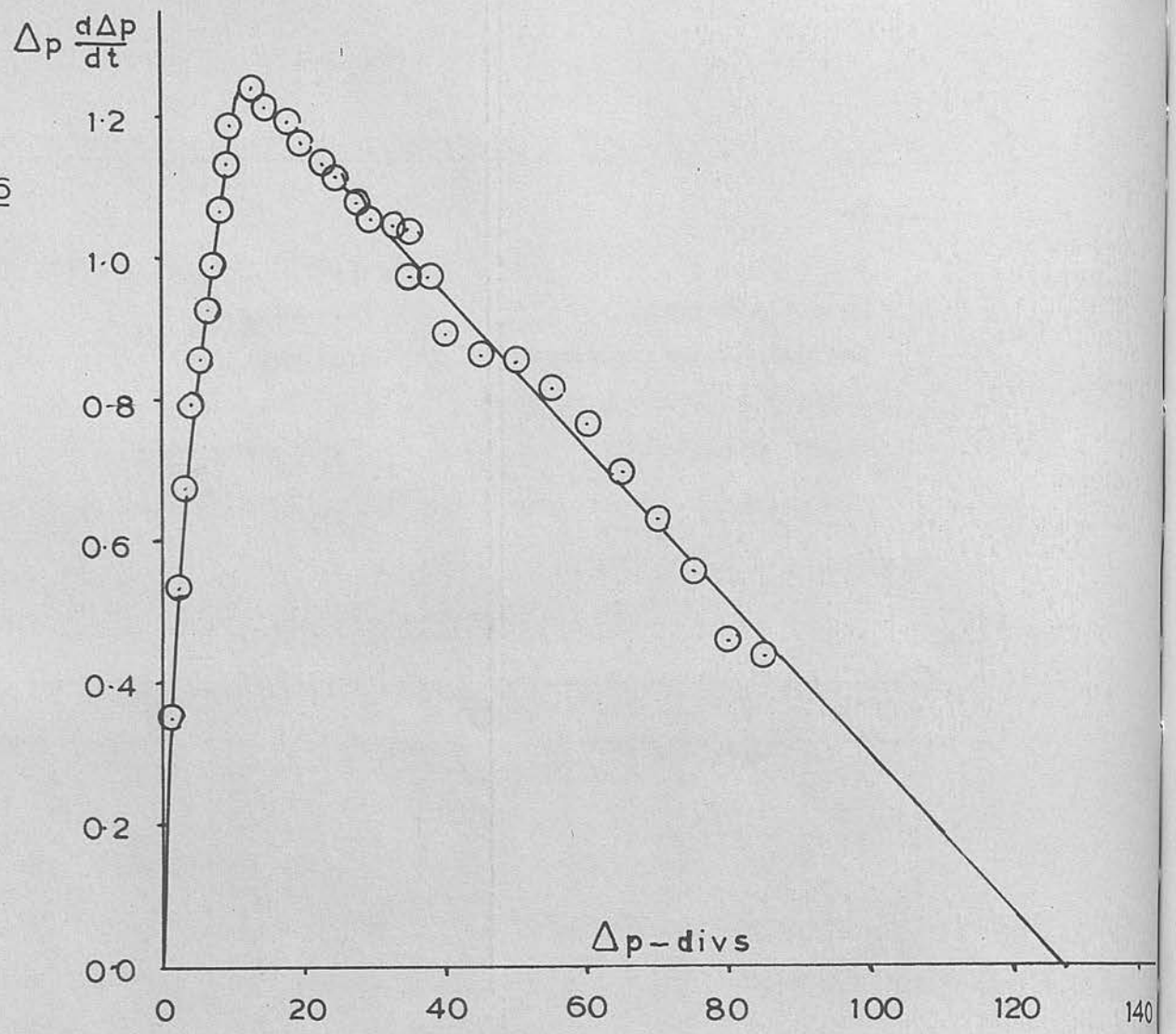

Δp dΔp/dt
1·2
1·0
0·8
0·6
0·4
0·2
0·0
Δp – divs
0
20
40
60
80
100
120
140

Fig 16

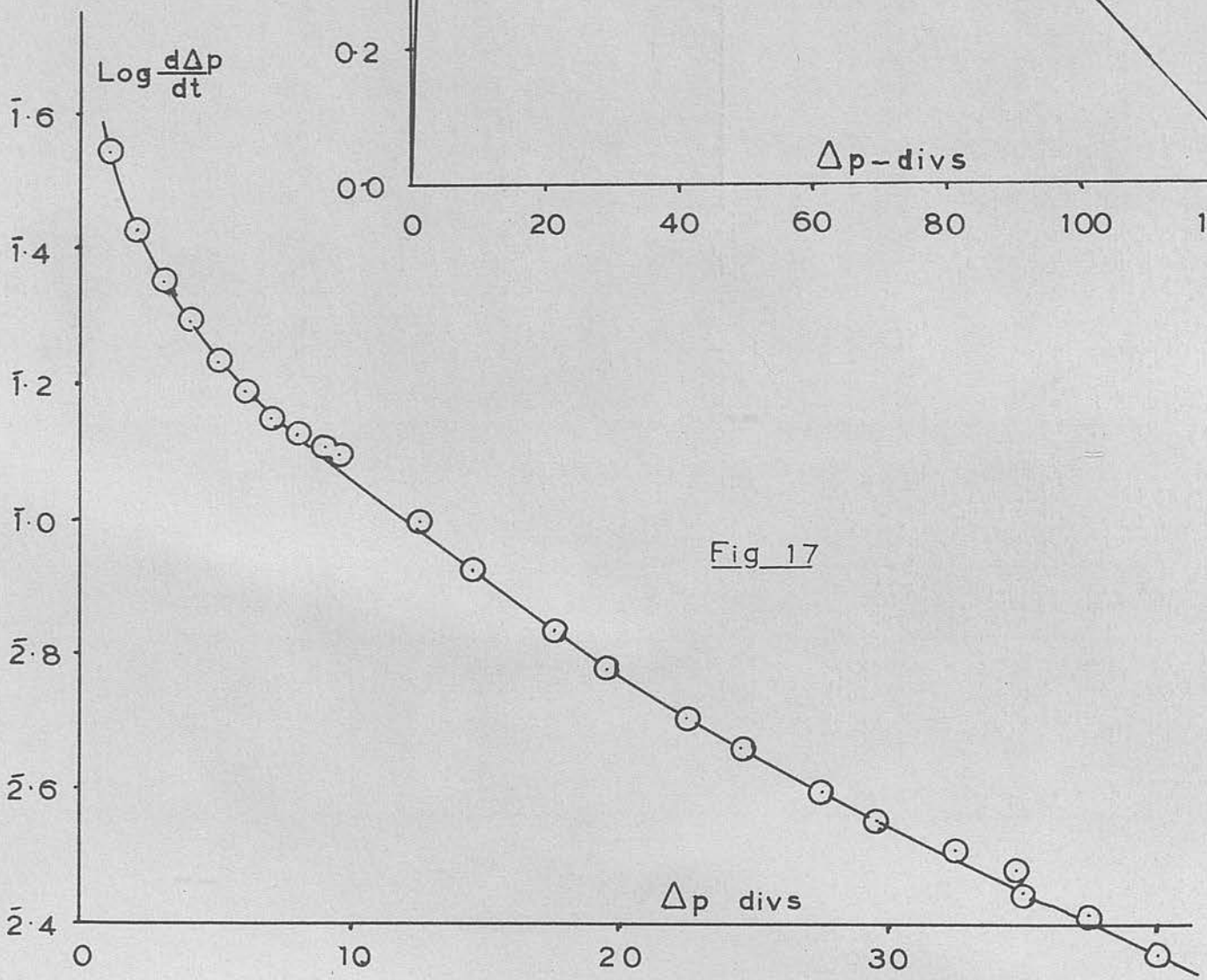

Log dΔp/dt
1̄·6
1̄·4
1̄·2
1̄·0
2̄·8
2̄·6
2̄·4
Δp divs
0
10
20
30

Fig 17

Table XII

Δp	$\Delta p.\frac{d\Delta p}{dt}$	Δp	$\Delta p.\frac{d\Delta p}{dt}$	Δp	$\Delta p.\frac{d\Delta p}{dt}$	Δp	$\Delta p.\frac{d\Delta p}{dt}$
1	0.351	9	1.134	27.5	1.078	50	0.850
2	0.534	9.5	1.189	29.5	1.053	55	0.813
3	0.675	12.5	1.239	32.5	1.042	60	0.761
4	0.792	14.5	1.215	34.5	1.037	65	0.696
5	0.855	17.5	1.190	35.0	0.973	70	0.628
6	0.924	19.5	1.169	37.5	0.971	75	0.556
7	0.987	22.5	1.132	40	0.899	80	0.456
8	1.064	24.5	1.116	45	0.859	85	0.434

Although, in the initial stages, a poor agreement was obtained with the Roginsky-Zeldovich equation there was the same general shape of the $\log\frac{d\Delta p}{dt}$ - Δp plot (Fig. 17) as was found with the uptake of oxygen from a pure oxygen atmosphere.

The extrapolated value of $\Delta p_{\infty}(\frac{d\Delta p}{dt} = 0)$, from Fig. 16, was 127 divs. and was equivalent to a pressure decrease of 170×10^{-6} moles/gm. This value compared very closely with that obtained for uptake of oxygen from a pure oxygen atmosphere. It can be stated that hydrogen, present in the oxygen, did not give rise to an abnormally large pressure decrease and it could be expected that only small amounts of water of the order of the observed pressure decrease would be present in the products.

Products.

(1) 24 hr. evacuation prior to illumination

$$\Delta_1 H_2O = 3.8\mu$$

(2) 24 hr. evacuation following illumination

$$\Delta_2 H_2O = 5.8\mu$$

$$\Delta CO_2 = 1.1\mu$$

(3) /

(3) 24 hr. evacuation following (2)

$$\Delta_3 H_2O = 2.0\mu$$
$$\Delta CO_2 = 0.0\mu$$

The amount of water produced by aging during the evacuation of the products amounted to 2.7μ.

Illumination then produced:-

$$\Delta H_2O = 5.8 - 2.7 = 3.1\mu$$
$$\Delta CO_2 = \quad = 1.1\mu$$

The pressure decrease was 91.0 divs. on illumination:-

$$\therefore \quad \Delta p = 6.71\mu$$

In this experiment the amount of products obtained was low in comparison to the pressure decrease. Again a small amount of CO_2 occurred in the products after illumination. The extent of the pressure decrease on illumination was the same as that for uptake of oxygen from a pure oxygen atmosphere and it was therefore probable that gaseous hydrogen does not enter into the process.

In the later stages ($\Delta p > 10$ divs.) of the photo process:-

$$\frac{d\Delta p}{dt} = K \left(\frac{\Delta_\infty p - \Delta p}{\Delta p} \right) \qquad \text{(Fig. 16)}$$

$$= -0.0108 \left(\frac{127 - \Delta p}{\Delta p} \right)$$

PHOTO-/

PHOTO-UPTAKE OF OXYGEN ON ACETONE BOUND FILMS

From two preliminary experiments on films 4 and 5 it became apparent that the photo-uptake of oxygen was accompanied by the slow gaseous evolution of CO_2 and that extrapolated values of $\Delta_\infty p$ could not be obtained by plotting $\Delta p \frac{d\Delta p}{dt}$ against Δp. By plotting antilog $\frac{d\Delta p}{dt}$ against $\frac{1}{\Delta p}$, however, the latter part of the pressure decrease appeared to be linear and capable of extrapolation. By this empirical method extrapolated decreases of films 4 and 5 were obtained.

Table XIII

	Film 4	Film 5
Wt. Sample II (after evacuation)	.0814 gms.	0.0125 gms.
Δp observed on illumination	22.9 μ	4.15 μ
$\Delta_\infty p$ from antilog $\frac{d\Delta p}{dt}$ - $\frac{1}{\Delta p}$ plot	363 μ/gm.	501 μ/gm.

After degassing the exposed films at 25°C for 24 hours no acetone was detected and the amounts of carbon dioxide detected were:-

	Film 4	Film 5
ΔCO_2	8.1 μ	1.55 μ

On the assumption that all the CO_2 produced photochemically would appear on evacuation it is reasonable to propose that if the film had been illuminated for an infinite time until the rate of oxygen uptake was zero then all the CO_2 produced would have diffused from the solid into the gas phase. The time of illumination of films 4 and 5 was very small in comparison with that required to reach zero rate of uptake and only fractional amounts of CO_2 were detected in the gas phase. Extrpolated values of $\Delta_\infty p$ must then be "scaled up" by the factor of $\frac{\Delta p + \Delta CO_2}{\Delta p}$ to obtain the extrapolated uptake of oxygen ($\Delta_\infty O_2$):-

	Film 4	Film 5
$\Delta_\infty O_2$	492 μ/gm.	689 μ/gm.

Although/

Although the extrapolated uptakes of oxygen are not in good agreement it is quite evident that the capacity for oxygen under illumination was very much larger when films were deposited from acetone. For film 4 the three evacuations produced:-

Table XIV

Prelim. (24 hrs.)	$\Delta_1 H_2O = 4.8\,\mu$
Products (24 hrs.)	$\Delta_2 H_2O = 28.2\,\mu$
	$\Delta CO_2 = 8.1\,\mu$
Final (24 hrs.)	$\Delta_3 H_2O = 3.0\,\mu$

The amount of water, (ΔH_2O), produced photochemically was thus 28.2 - 3.8 = 24.4 μ.

The observed pressure decrease was $\Delta p = 22.9\,\mu$

Ratio $\Delta p : \Delta H_2O : \Delta CO_2 = 122.9 : 24.4 : 8.1$

$= 1.00 : 1.07 : 0.35$

$= 2.83 : 3.01 : 1.00$

CO_2 and water are produced in the ratio of 1:3. The amount of oxygen, (ΔO_2), consumed in this process was not accurately known but was more than 22.9 μ since no allowance has been made to compensate for the production of gaseous CO_2. ΔO_2 must also be less than ($\Delta p + \Delta CO_2$) = 31.0 μ and lies between the limits 22.9 and 31.0 μ.

$\therefore \quad \Delta CO_2 : \Delta O_2 = 1.00 : 2.83 \longrightarrow 3.83$

For film 5 the outside limits of O_2 were 4.15 and 5.7 .

$\therefore \quad \Delta CO_2 : \Delta O_2 = 1.00 : 2.68 \longrightarrow 3.72$

Film 6. Acetone bound.

Wt. Sample II/

Wt. Sample II	0.0860 gms. (wt. after evacuation)
Reaction volume	28.6 mls.
Initial oxygen pressure	67 mm.
Guage sensitivity	0.0230 mm.

Film 6 was illuminated in the usual way, i.e. at the film gas interface for 460 mins. then allowed to stand in the dark for a further 960 mins.

Illumination of the reverse side (i.e. glass-film interface), was carried out for 446 mins. The reason behind this procedure was to establish the validity of the extrapolated value of Δp_∞ by the antilog $\frac{d\Delta p}{dt} - \frac{1}{\Delta p}$ plot. It was hoped that the difference in the extrpolated values would be equal to the amount of pressure decrease observed during the first illumination.

Table XV

Pressure decrease (Δp) on illuminating film 6, in oxygen, as a function of time (t mins.).

t	Δp	t	Δp	t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	8	26.3	20	50.5	51	95.5	153	197.0	316	316.7
½	3.0	9	28.9	22	54.3	60	106.3	160	204.9	333	326.8
1	5.1	10	31.0	23	55.9	69	116.7	170	213.1	366	345.9
1½	7.1	11	33.1	24	57.2	74	122.5	188	227.4	395	362.8
2	9.2	13	37.2	26	60.3	85	134.5	195	233.2	407	369.7
2½	11.1	14	39.2	29	64.7	92	141.9	226	256.1	453	372.9
3	13.0	15	41.3	31	67.8	100	150.1	236	263.4	460	376.7
4	15.9	16	43.1	34	72.4	113	162.2	266	280.2	Illum.	
5	18.8	17	45.1	37	76.6	120	169.0	276	290.7	ceased	
6	21.3	18	46.9	40	80.7	132	180.2	287	297.8	Dark uptake	
7	23.9	19	48.6	47	90.2	141	188.3	302	307.6	1400	398.7

Table XVa/

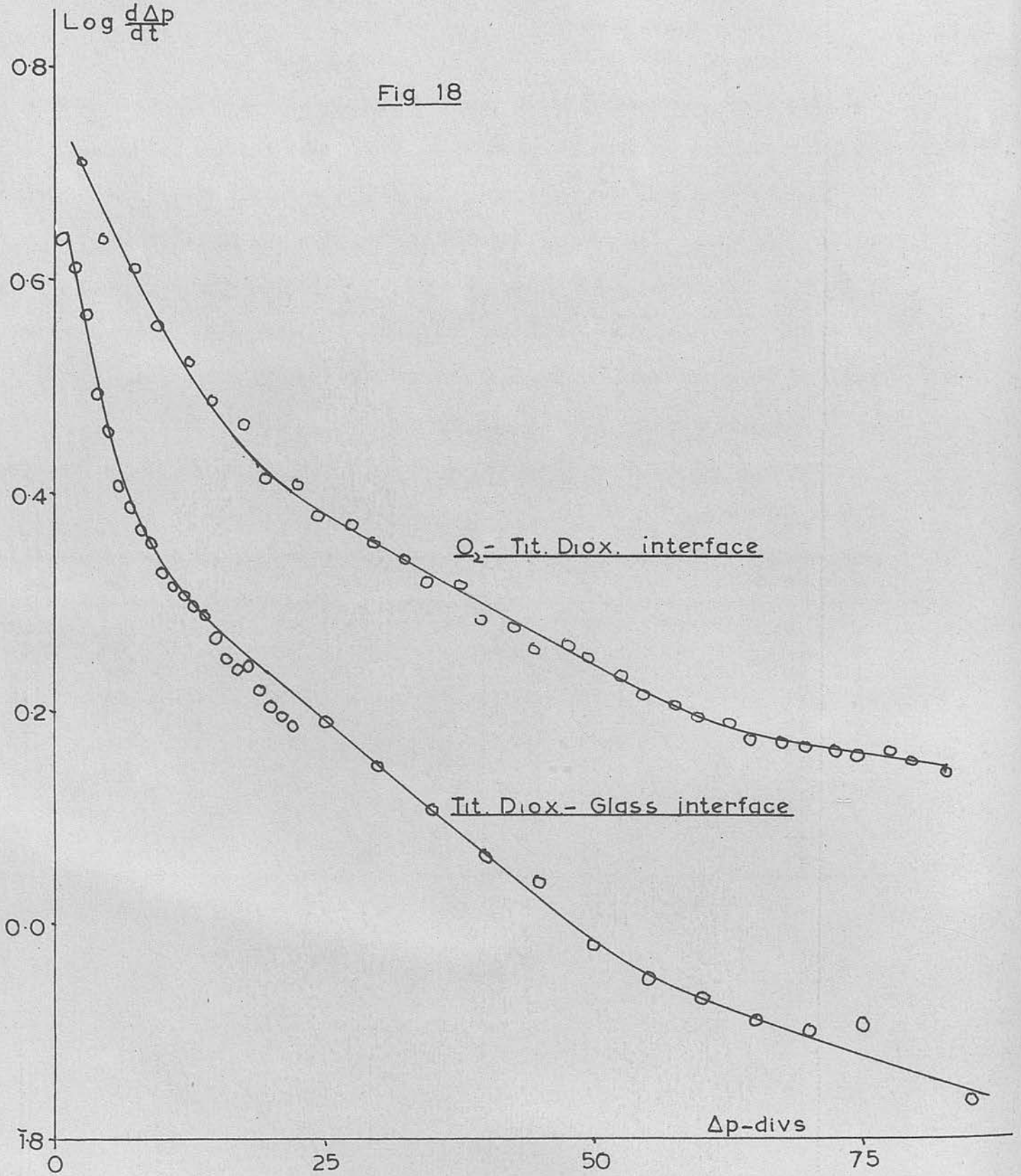

Log $\frac{d\Delta p}{dt}$
0·8
0·6
0·4
0·2
0·0
$\bar{1}$·8
0
25
50
75
Δp-divs
O_2- Tit. Diox. interface
Tit. Diox.- Glass interface

Fig 18

Table XVa

Illumination continued on reverse side of film.

t	Δp'	t	Δp'	t	Δp'	t	Δp'	t	Δp'	t	Δp'
0	0.0	8	18.8	18	33.7	81	88.4	171	141.4	329	214.0
½	1.8	9	20.4	19	34.8	89	92.7	190	151.0	344	220.0
1	4.0	10	21.7	20	35.0	101	100.6	204	158.9	359	225.5
1½	5.4	11	23.0	26	42.7	107	104.6	214	163.7	394	238.2
2½	7.9	12	24.5	27	43.7	110	107.6	226	168.6	406	242.8
3	9.0	13	26.3	32	49.0	112	109.6	243	177.5	421	248.1
4	11.4	14	27.7	39	56.4	127	116.6	266	187.5	437	253.8
5	13.1	15	29.2	47	62.3	136	121.7	280	194.6	446	256.8
6	14.9	16	31.3	57	71.0	147	128.0	297	201.0	Illumination	
7	17.0	17	32.6	70	82.0	157	134.5	312	207.1	ceased.	

Tables XVI and XVIa. Derived values from Tables XV and XVa.

Table XVI

Δp	$\frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	$\text{antilog} \frac{d\Delta p}{dt}$	$\frac{1}{\Delta p}$
2.5	5.13	0.710	82.5	1.37		
4.5	4.35	.639	84.5	1.33		
7.5	4.08	.611	87.5	1.33		
9.5	3.60	.556	90	1.29		
12.5	3.33	.522	95	1.25		
14.5	3.06	.486	100	1.235		
17.5	2.90	.467	105	1.20		
19.5	2.60	.415	110	1.18		
22.5	2.56	.408	120	1.13		
24.5	2.40	.380	130	1.08	12.0	0.00769
27.5	2.35	.371	140	1.03	10.7	.00714
29.5	2.26	.354	150	1.01	10.2	.00667
32.5	2.18	.339	160	0.99	9.77	.00625
34.5	2.08	.318	170	0.944	8.79	.00588
37.5	2.07	.316	180	0.91	8.13	.00555
39.5	1.92	.283	190	0.876	7.52	.00526
42.5	1.88	.274	200	0.846	7.02	.00500
44.5	1.80	.255	210	0.826	6.70	.00476
47.5	1.81	.258	220	0.800	6.31	.00455
49.5	1.76	.246	230	0.781	6.04	.00435
52.5	1.70	.230	240	0.747	5.59	.00417
54.5	1.63	.212	250	0.735	5.43	.00400
57.5	1.59	.201	260	0.709	5.12	.00385
59.5	1.55	.190	270	0.695	4.96	.00370
62.5	1.53	.185	280	0.685	4.84	.00357
64.5	1.48	.170	290	0.665	4.62	.00345
67.5	1.47	.167	300	0.645	4.42	.00333
69.5	1.46	.164	320	0.615	4.12	.00313
72.5	1.44	.158	340	0.597	3.95	.00294
74.5	1.43	.155	360	0.563	3.66	.00278
77.5	1.44	.158				
79.5	1.41	.149				

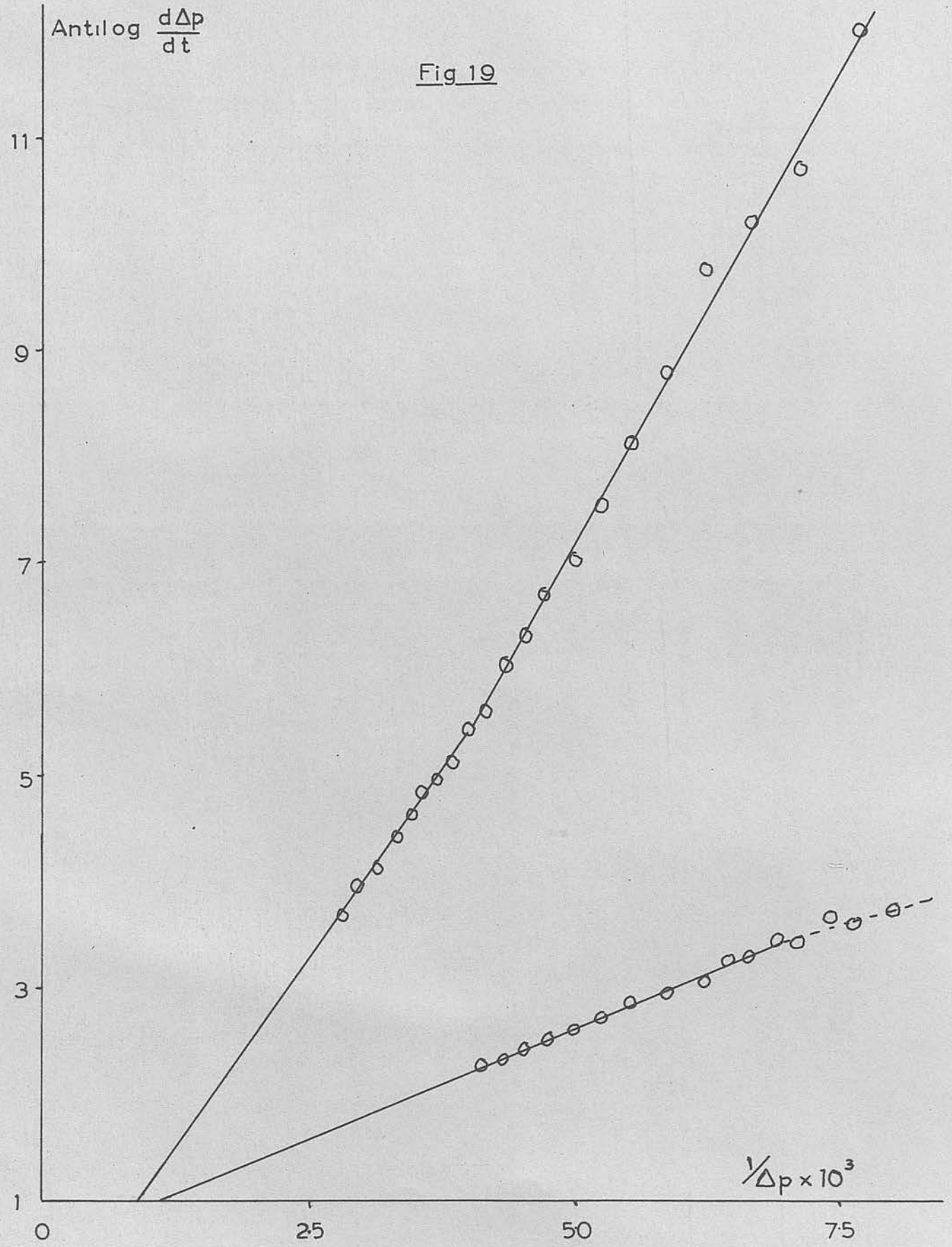


Fig 19

Table XVIa

$\Delta p'$	$\frac{d\Delta p'}{dt}$	$\log \frac{d\Delta p'}{dt}$	$\Delta p'$	$\frac{d\Delta p'}{dt}$	Antilog $\frac{d\Delta p'}{dt}$	$\frac{1}{\Delta p'}$
1	4.38	0.639	50	0.95		$\bar{1}.978$
2	4.08	.611	55	0.89		$\bar{1}.949$
3	3.70	.568	60	0.85	$\log \frac{d\Delta p}{dt}$	$\bar{1}.929$
4	3.12	.494	65	0.81		$\bar{1}.908$
5	2.88	.459	70	0.79		$\bar{1}.898$
6	2.56	.408	75	0.80		$\bar{1}.803$
7	2.38	.377	85	0.68		$\bar{1}.833$
8	2.32	.366	95	0.645	4.416	0.01053
9	2.27	.356	105	0.596	3.945	.00952
10	2.13	.328	115	0.578	3.784	.00867
11	2.06	.314	125	0.572	3.733	.00800
12	2.02	.305	135	0.562	3.65	.00741
13	1.98	.297	145	0.538	3.45	.00690
14	1.94	.288	155	0.513	3.26	.00645
15	1.85	.267	131.3	0.556	3.60	.00764
16	1.76	.246	141.3	0.534	3.42	.00710
17	1.73	.238	151.3	0.517	3.29	.00664
18	1.74	.241	161.3	0.485	3.06	.00622
19	1.65	.218	171.3	0.469	2.94	.00586
20	1.59	.201	181.3	0.457	2.86	.00553
21	1.56	.193	191.3	0.435	2.72	.00524
22	1.52	.182	201.3	0.415	2.60	.00498
25	1.54	.188	211.3	0.400	2.51	.00474
30	1.40	.146	221.3	0.384	2.42	.00453
35	1.28	.107	231.3	0.368	2.33	.00433
40	1.15	.061	241.3	0.358	2.28	.00415
45	1.09	.037				

From Fig. 18 the initial stages of the uptake show the same approximate agreement to the Roginsky-Zeldovich equation as did the uptake from a hydrogen-oxygen gas mixture on to a water bound film. Plots of antilog $\frac{d\Delta p}{dt}$ against $\frac{1}{\Delta p}$ in Fig. 19 exhibit linearity and the extrapolated values are:-

First illumination $\Delta_\infty p$ = 1124 divs. (463μ/g.)

Second illumination in reverse side $\Delta_\infty p'$ = 935 divs. (385μ/g.)

The difference between the two is 189 divs. which is not equal to the value of Δp obtained from the first illumination (= 398.7 divs.). From this it would appear that the uptake on the reverse side would be larger than expected. However, it must be borne in mind that the reverse side was a glass-film/

film interface and diffusion effects would be introduced. The CO_2 formed would not easily escape into the gas phase since it had to diffuse through the whole thickness of the film. Since the rate of the uptake of oxygen was reasonably large it is probable that it was surface adsorbed in a mobile state and easily migrated to surface sites. The extrapolated value of $\Delta_\infty p$ from the first illumination was 463 μ/gm. and from the reverse side $\Delta_\infty p'$ = 385 μ/gm.

Products on evacuation : acetone nil

Prelim. (24 hrs.) $\Delta_1 H_2O$ = 5.8 μ

Products (24 hrs.) $\Delta_2 H_2O$ = 16.0 μ (Δp = 14.15 μ

ΔCO_2 = 4.55 μ ($\Delta p'$ = 8.96 μ

Final (24 hrs.) $\Delta_3 H_2O$ = 1.6 μ

Allowance for water formed thermally (aging) $\Delta' H_2O$ = 2.8 μ

Products due to illumination:-

ΔH_2O = 16.0 - 2.8 = 13.2 μ

ΔCO_2 = 4.55 μ

ratio $\Delta CO_2 : \Delta H_2O$ = 1.00 : 2.90

Again carbon dioxide and water obtained in the ratio 1:3.

The ratio (1) $\Delta p : \Delta CO_2 : \Delta H_2O$ = 14.15 : 4.55 : 13.2

= 3.11 : 1.00 : 2.90

and (2) $(\Delta p + \Delta p') : \Delta CO_2 : \Delta H_2O$ = 23.11 : 4.55 : 13.2

= 5.08 : 1.00 : 2.90

The ratio (1) is in good agreement with films 4 and 5 and suggests that illumination of the film at the glass-film interface caused an entrapping of gaseous products, with a correspondingly higher observed pressure decrease. If the first illumination was entirely responsible for the production of the measured CO_2 then the extrapolated oxygen uptake would be 463 x $\frac{\Delta p + CO_2}{\Delta p}$

$$\Delta_\infty O_2 = 463 \times \frac{18.7}{14.15} = 611 \mu/gm.$$

and/

and if the second illumination was not responsible for any gaseous products then the measured uptake would have been entirely oxygen. $\Delta_{\infty} p' = \Delta_{\infty} O_2' = 385 \mu/gm.$ The oxygen uptake during the first illumination would have been between 14.15 and 18.7 μ, i.e. between Δp and $\Delta p + \Delta CO_2 = 165$ to $218 \mu/gm.$ On this basis the total extrapolated oxygen uptake from the second illumination plus the oxygen uptake during the first illumination was between 385 + 165 and 385 + 218, i.e. between 550 and $603 \mu/gm.$ If most of the CO_2 produced (1st illumination) was in the gas phase, as was most likely, then a fairly good agreement within experimental limits is obtained.

First illumination $\Delta_{\infty} O_2 = 611 \mu/gm.$

Second illumination $\Delta_{\infty} O_2' + \Delta O_2$ (First illum.) $= 603 \mu/gm.$

Summary of Oxygen Uptake on Acetone Bound Films

(1) Illumination of an acetone bound film in oxygen has shown a much larger oxygen uptake than has been observed with a water bound film.

$\Delta_{\infty} O_2$ for water bound (film 2) $= 176 \mu/gm.$

$\Delta_{\infty} O_2$ for acetone bound (film 4) $= 492 \mu/gm.$

do. do. (film5) $= 689 \mu/gm.$

do. do. (film 6) $= 611 \mu/gm.$

$\Delta_{\infty} O_2$ average for acetone bound film $= 597 \mu/gm.$ ($600 \mu/gm.$)

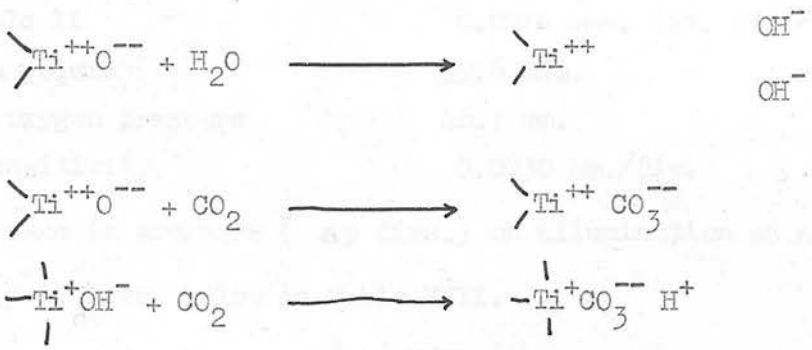
(2) The uptake of oxygen was attended by the production of water and carbon dioxide. The ratio of $CO_2 : H_2O$ in the evacuation products was 1:3.

(3) Illumination at the film-oxygen interface, may have been responsible for the production of gaseous products. By assuming the extreme case in film 6 it has been shown that illumination at the film-glass interface may have resulted in the gaseous products being entrapped.

(4) The relative ease with which oxygen was photosorbed at the film-glass interface would suggest a migratory surface adsorption of oxygen. The assumed non appearance of gaseous products would suggest localised adsorption by weak

bonding/

bonding, e.g. hydrogen bonding or hydroxyl group formation on the surface with water:-



(1)

(2)

Space restrictions would render the removal of H_2O and CO_2 at the film-glass interface extremely difficult at 25°C by a diffusion process.

(5) The large extent to which oxygen was photosorbed on acetone bound films and also the stoichiometric ratio of the products water and carbon dioxide would suggest the possibility of an oxidation of chemisorbed acetone.

(6) Since the films examined had a definite thickness there might probably be some regions that remained totally "in the dark" during illumination. If this was so then the extrapolated value of Δp_∞ would depend on the weight and thickness of the film. Such a consideration might be applicable to film 6 to provide an alternative explanation of the extrapolated value of Δp_∞. The production of gaseous CO_2, however, must be taken into account.

From the summary above the oxygen uptake on a film bound with methyl ethyl ketone was suggested and examined next. It was possible that the oxygen uptake would be greater than that for acetone-bound films.

In order to support the results from films 4, 5 and 6, a stoichiometric ratio between ΔCO_2 and ΔH_2O was looked for in the evacuation products obtained after illumination.

UPTAKE OF OXYGEN ON A METHYL ETHYL KETONE BOUND FILM

Film 7

Wt. Sample II	0.0214 gms. (wt. after evacuation)
Reaction volume	59.6 mls.
Initial oxygen pressure	48.1 mm.
Guage sensitivity	0.0230 mm./div.

The decrease in pressure (Δp divs.) on illumination as a function of time (t mins.) is given below in Table XVII.

Table XVII

t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	18	5.4	257	37.1	786	83.0
0.5	0.4	19	5.7	279	39.2	798	83.3
1.0	0.7	20	5.8	289	40.7	1483	87.2
1.5	0.8	21	5.9	313	41.9	1570	88.3
2.0	1.0	23	6.4	337	43.7	1716	90.1
3	1.3	24	6.8	346	44.5	1837	92.1
4	1.7	29	7.8	363	45.7	1935	93.9
5	2.0	33	8.6	373	46.5	2130	96.5
6	2.5	38	9.6	387	47.3	2838	104.6
7	2.6	48	11.6	418	49.5	2913	105.4
8	2.7	60	13.6	490	53.8	3039	106.4
9	3.0	71	15.3	593	59.7	3188	107.6
10	3.4	82	17.0	604	60.0	3260	108.3
11	3.7	89	18.0	629	61.3	3389	109.6
12	3.8	106	20.7	656	62.5	4278	116.2
13	4.0	120	22.5	674	63.0	4391	116.4
14	4.6	157	26.9	689	79.0	4469	116.8
15	4.8	182	29.6	715	80.0	4515	117.1
16	4.8	202	31.7	749	81.3	illumination ceased	
17	4.9	235	35.0	774	81.4		

Derived values from Table XVII are given in Table XVIII.

Table XVIII /

Fig 20

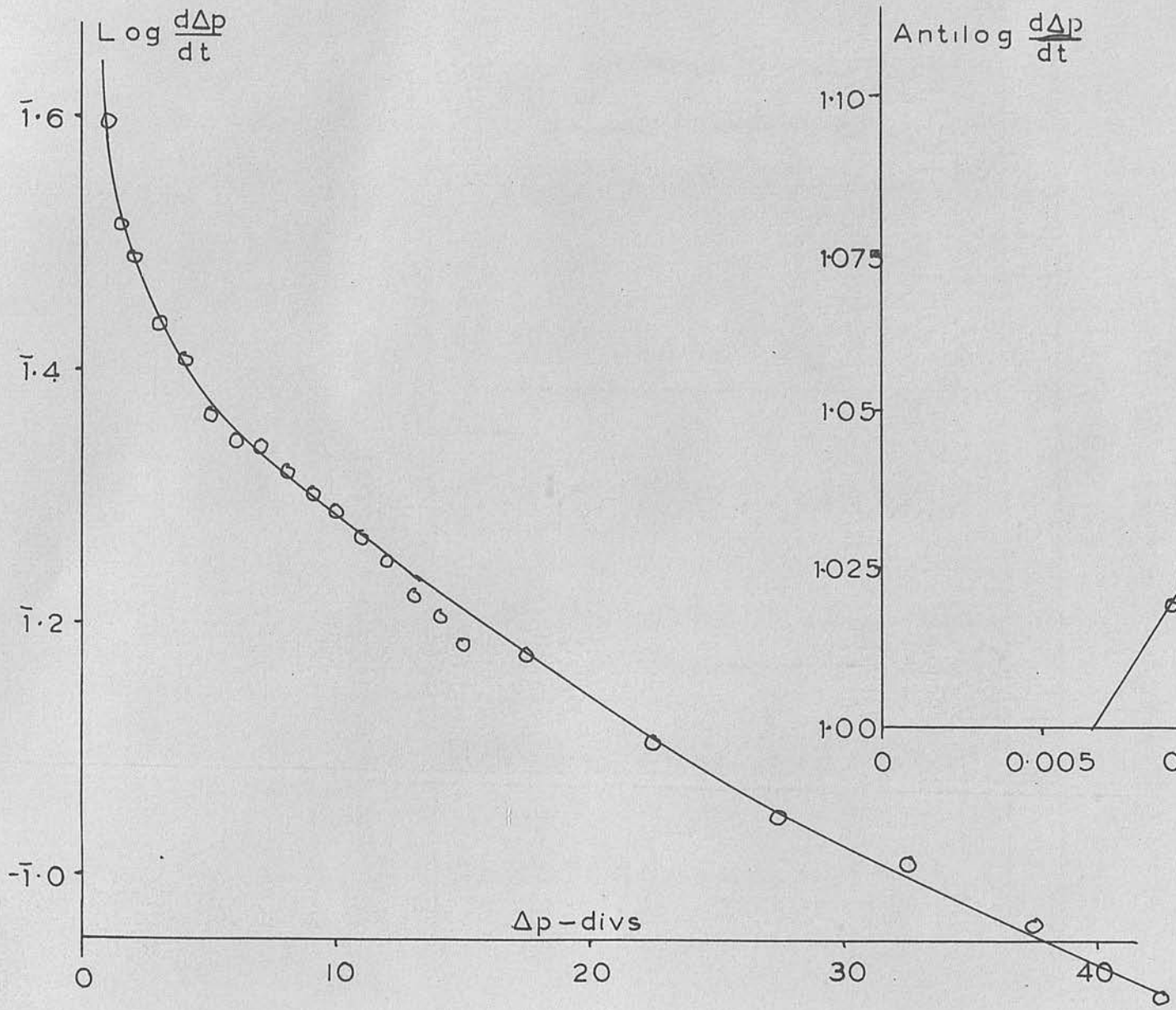

Log dΔp/dt
1̄·6
1̄·4
1̄·2
-1̄·0
Δp-divs
0
10
20
30
40

Fig 21

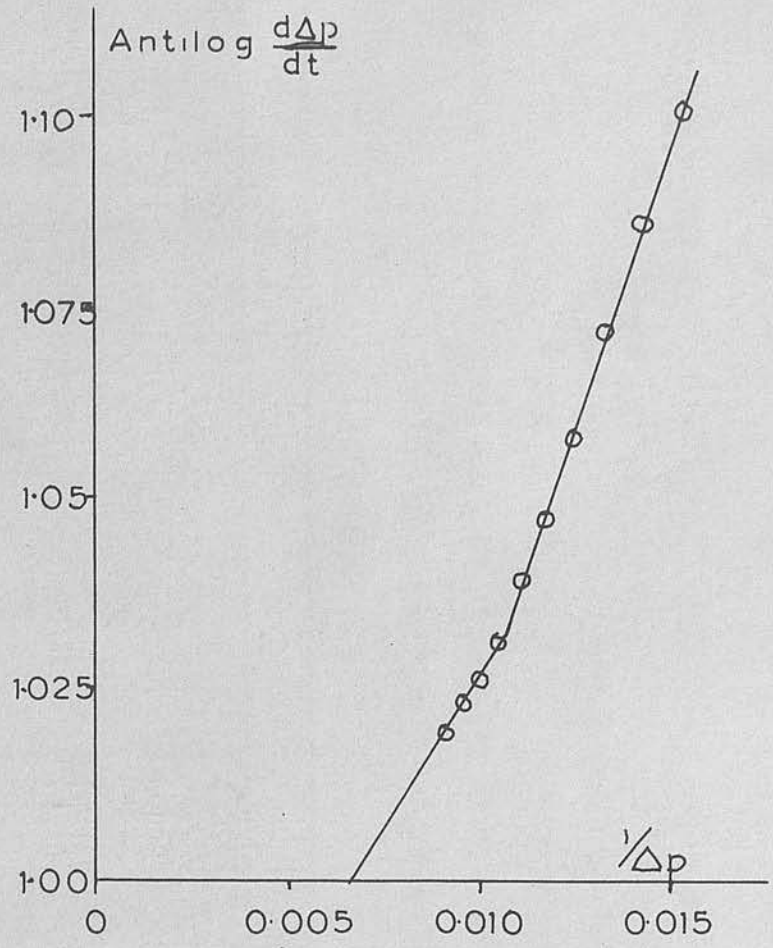

Antilog dΔp/dt
1·10
1·075
1·05
1·025
1·00
1/Δp
0
0·005
0·010
0·015

Table XVIII

Δp	$\frac{d\Delta p}{dt}$	$\log_{10} \frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	antilog $\frac{d\Delta p}{dt}$	$\frac{1}{\Delta p}$
1	0.394	$\bar{1}.596$	47.5	0.0690		
1.5	0.328	$\bar{1}.516$	52.5	0.0588		
2	0.308	$\bar{1}.489$	57.5	0.0526		
3	0.274	$\bar{1}.436$	62.5	0.0436		
4	0.255	$\bar{1}.407$	65	0.0421	1.102	0.0154
5	0.231	$\bar{1}.364$	70	0.0357	1.086	0.0143
6	0.221	$\bar{1}.344$	75	0.0301	1.072	0.0133
7	0.218	$\bar{1}.339$	80	0.0246	1.058	0.0125
8	0.208	$\bar{1}.318$	85	0.0197	1.047	0.0118
9	0.200	$\bar{1}.301$	90	0.0165	1.039	0.0111
10	0.194	$\bar{1}.288$	95	0.0137	1.031	0.0105
11	0.185	$\bar{1}.267$	100	0.0113	1.026	0.0100
12	0.177	$\bar{1}.248$	105	0.0897	1.023	0.0095
13	0.167	$\bar{1}.220$	110	0.0081	1.019	0.0091
15	0.153	$\bar{1}.182$				
17.5	0.149	$\bar{1}.173$				
22.5	0.127	$\bar{1}.104$				
27.5	0.111	$\bar{1}.045$				
32.5	0.102	$\bar{1}.009$				
37.5	0.091	$\bar{2}.959$				
42.5	0.080	$\bar{2}.903$				

Again, as before (Figs. 17 and 18) the Roginsky-Zeldovich plot was in the same form as that observed with the oxygen uptake on an acetone bound film.

Fig. 21, which is of the same form as Fig. 19 (1st illumination), gives a linear plot between antilog $\frac{d\Delta p}{dt}$ and $\frac{1}{\Delta p}$. Extrapolation to zero rate shows the ultimate pressure decrease to be 149 divs. equivalent to 515 μ/gm. The observed pressure decrease, Δp, was 117.1 divs. equivalent to 8.65 μ moles.

Products. Methyl-ethyl Ketone Nil

Prelim. evac. (24 hrs.)	$\Delta_1 H_2O$	= 2.1 μ
Products (a) gas phase	$\Delta_g CO_2$	= 4.94 μ
(b) exhaustive 24 hr. evac.	$\Delta_2 CO_2'$	= 0.8 μ
	$\Delta_2 H_2O$	= 12.3 μ
Final evac. (24 hrs.)	$\Delta_3 H_2O$	= 1.1 μ

Allowance/

Allowance for aging during illumination $\Delta' H_2O = 1.5 \mu$

Water produced photochemically $\Delta H_2O = 12.3 - 1.5 = 10.8 \mu$

Total CO_2 produced $\Delta CO_2 = \Delta_g CO_2 + \Delta CO_2' = 5.74 \mu$

Ratio $\Delta CO_2 : \Delta H_2O = 1.00 : 1.88$

The observed pressure decrease (Δp) was 8.65μ and the amount of CO_2 in the gas phase ($\Delta_g CO_2$) was 4.94μ. On the assumption that the water produced gave a negligible vapour pressure due to adsorption the total reduction in the oxygen pressure on illumination was:-

$$\Delta O_2 = 8.65 + 4.94 = 13.59 \mu .$$

Ratio $\Delta O_2 : \Delta CO_2 : \Delta H_2O = 13.59 : 5.74 : 10.8$

$$= 5.00 : 2.18 : 3.98$$

The ratio of $\Delta O_2 : \Delta CO_2 : \Delta H_2O$ was stoichiometric and indicated a photochemical process:-

$$5O_2 + (X\text{-ads.}) \xrightarrow[\lambda < 4000\text{A}]{\text{light}} 2CO_2 + 4H_2O + (Y\text{-ads.})$$

with X being the adsorbed reactant and Y the adsorbed oxidation product.

The extrapolated value of $\Delta_\infty p$ was 515μ moles/gm. It was assumed, (as with the acetone bound films), that after an infinite time of illumination when the rate of oxygen uptake would be zero the extrapolated oxygen uptake ($\Delta_\infty O_2$) was:-

$$\Delta_\infty O_2 = \Delta_\infty p \times \frac{\Delta p + \Delta CO_2}{\Delta p}$$

$$= 515 \times \frac{8.65 + 5.74}{8.65}$$

$$\Delta_\infty O_2 = 855 \mu/\text{gm.}$$

Brief Summary of Oxygen Uptake on Methyl-Ethyl Keton Bound film

(1) A stoichiometric ratio has been observed between the oxygen uptake (ΔO_2), and the products carbon dioxide (ΔCO_2) and water (ΔH_2O).

$\Delta O_2 : \Delta CO_2 : \Delta H_2O = 5.00 : 2.18 : 3.98 = 5 : 2 : 4$

(2) The extrapolated oxygen uptake was 855 μ/gm.

SUMMARY OF OXYGEN UPTAKE ON VARIOUS FILMS

Table XIX

Film 2 - water bound	ΔO_2	= 1 x 176 μ/gm.
Film 3 - water bound ($O_2 + H_2$)	Δp	= 1.x 170 μ/gm.
Films 4, 5 and 6 - acetone bound	ΔO_2 (average)	= $3\frac{1}{2}$ x 171 μ/gm.
Film 7 - methyl-ethyl ketone bound	ΔO_2	= 5 x 171 μ/gm.

From the above Table is it clear that there is a definite correlation between the various processes. It is assumed that there were 171 μ moles unit sites per gram of Sample II then one site would have been responsible for the uptake of 1 molecule of oxygen in film 2, one gas molecule in film 3, $3\frac{1}{2}$ oxygen molecules in films 4, 5 and 6 and five oxygen molecules in film 7. Taking into consideration the products concerned the following schemes are postulated:-

Films 1 and 2 - water bound:-

$$(\text{site}) + O_2 \xrightarrow{\text{light}} (\text{oxid. site}) + 2H_2O$$

Films 4, 5 and 6 - acetone bound:-

$$(CH_3.CO.CH_3 + \text{site}) + 3\tfrac{1}{2}O_2 \xrightarrow{\text{light}} (C_2O_3 + \text{site}) + CO_2 + 3H_2O$$

Film 7 - methyl-ethyl ketone bound:-

$$(CH_3CO.C_2H_3 + \text{site}) + 5O_2 \xrightarrow{\text{light}} (C_2O_3 + \text{site}) + 2CO_2 + 4H_2O$$

PHOTO-/

PHOTO-UPTAKE of NITRIC OXIDE

Having obtained a correlation, between the oxygen uptake on water, acetone and methyl-ethyl ketone bound films, is it possible that it may also extend to the uptake of nitric oxide?

Film 8

Wt. Sample II	0.0634 gms. (wt. after evacuation)
Reaction volume	59.6 mls.
Initial nitric oxide pressure	75.7 mm.
Guage sensitivity	0.0230 mm/div.

As was observed by Kennedy (13) a relatively small slow "dark" (thermal) uptake of nitric oxide occurred immediately on contact with the titanium dioxide film. The actual pressure decrease observed with film 8 is given below in Table XX.

Table XX

t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	11	2.3	35	6.1	117	11.5
1	0.1	12	2.6	38	6.2	138	12.5
2	0.1	13	2.8	42	6.9	155	13.1
3	0.15	14.5	3.1	54	7.9	168	13.3
4	0.4	16.5	3.3	59	8.2	208	14.1
6	1.1	21	4.0	65	8.8	232	14.9
7	1.3	22	4.1	69	9.0	245	15.3
8	1.5	25	4.7	82	9.9	1200	41.0
9	1.9	28.5	5.1	92	10.4		
10	2.2	32	5.8	109	11.1		

Derived values given in Table XXI showed the "dark" uptake to obey the Roginsky-Zeldovich equation, i.e. indicating chemisorption. See Fig. 22.

Table XXI/

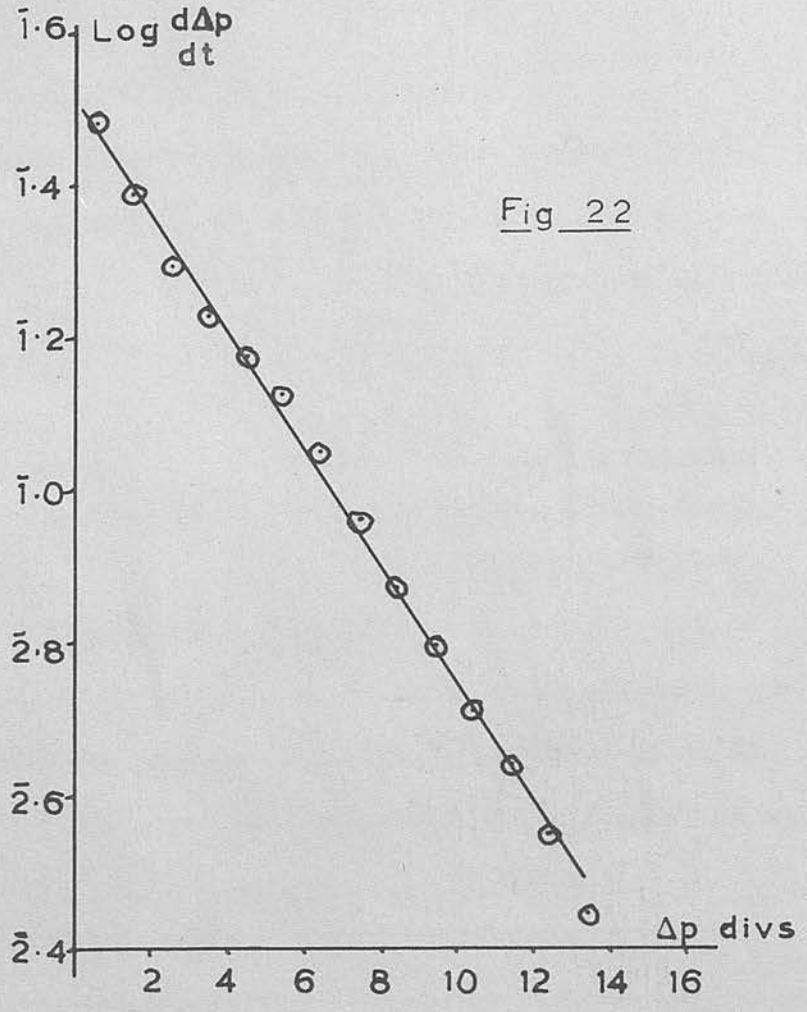

Log dΔp/dt
$\bar{1}\cdot6$
$\bar{1}\cdot4$
$\bar{1}\cdot2$
$\bar{1}\cdot0$
$\bar{2}\cdot8$
$\bar{2}\cdot6$
$\bar{2}\cdot4$
Δp divs
2 4 6 8 10 12 14 16

Fig 22

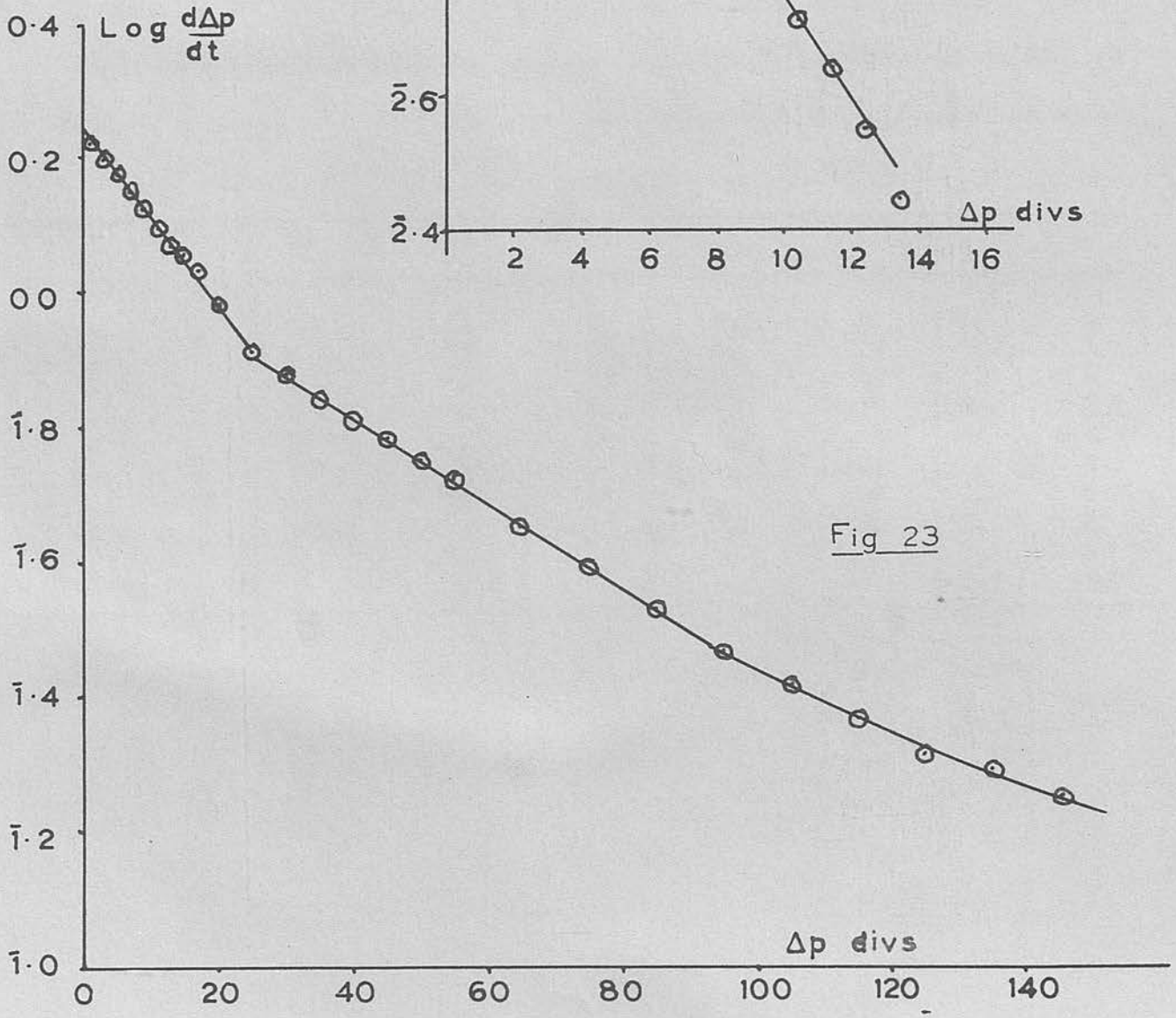

Log dΔp/dt
0·4
0·2
0 0
$\bar{1}\cdot8$
$\bar{1}\cdot6$
$\bar{1}\cdot4$
$\bar{1}\cdot2$
$\bar{1}\cdot0$
Δp divs
0 20 40 60 80 100 120 140

Fig 23

Table XXI

Δp	$\frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$
0.5	.303	$\bar{1}.481$	7.5	0.0918	$\bar{2}.963$
1.5	.244	$\bar{1}.387$	8.5	0.0741	$\bar{2}.870$
2.5	.196	$\bar{1}.292$	9.5	0.0625	$\bar{2}.796$
3.5	.167	$\bar{1}.227$	10.5	0.0513	$\bar{2}.710$
4.5	.149	$\bar{1}.173$	11.5	0.0435	$\bar{2}.638$
5.5	.132	$\bar{1}.124$	12.5	0.0354	$\bar{2}.549$
6.5	.112	$\bar{1}.049$	13.5	0.0278	$\bar{2}.444$

After 1200 mins. the rate of the "dark" uptake was found to have diminished to practically zero and the film was then illuminated. Table XXII gives the pressure decrease on illumination (Δp divs.) as a function of time (t mins.)

Table XXII

t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	13	17.05	174	95.7	1526	266.6
0.5	0.3	14	18.05	195	101.6	1538	267.4
1	1.1	15	18.7	217	107.5	1559	268.7
1.5	2.0	16	20.0	229	110.4	1586	270.1
2	2.8	17	20.9	274	121.5	1610	272.0
2.5	3.6	18	21.9	296	125.4	1636	273.6
3	4.2	19	22.9	309	128.1	1656	274.6
3.5	5.1	20	23.8	316	129.5	1699	277.5
4	5.8	21	24.9	339	134.3	1751	279.5
4.5	6.4	22	26.0	381	142.6	1759	280.9
5	7.1	23	26.4	402	145.6	1780	282.2
5.5	7.9	27	28.7	435	151.3	1831	284.9
6	8.5	30	32.2	472	157.3	1912	290.1
6.5	9.2	36	35.8	483	159.4	2916	338.6
7	10.0	42	39.7	486	160.1	2920	338.7
7.5	10.6	51	45.7	503	162.5	2932	339.1
8	11.2	65	53.4	506	163.2	2944	339.9
8.5	11.8	77	59.7	1440	260.8	2950	339.9
99	12.0	97	69.0	1445	261.0	2956	340.2
9.5	12.7	106	72.8	1455	261.9	2969	341.5
10	13.1	117	76.8	1469	262.7	2986	341.5
11	14.7	129	81.4	1475	263.2	3002	342.4*
12	16.0	152	89.0	1503	264.8	4000	347.8

* Illumination discontinued.

Derived values are given below in Table XXIII.

Table XXIII/

Fig 24

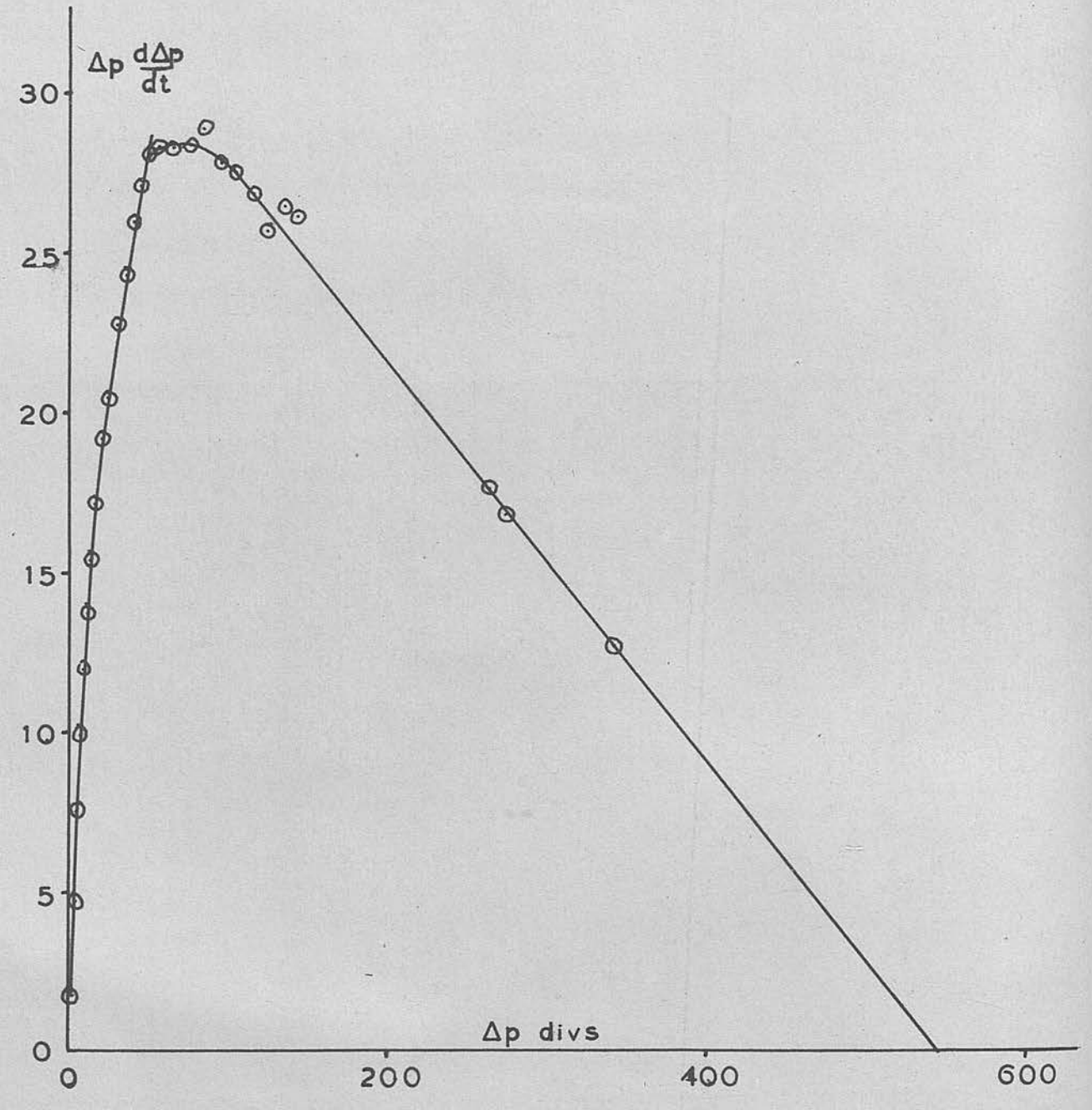


Table XXIII

Δp	$\frac{d\Delta p}{dt}$	$\Delta p \frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	$\Delta p \frac{d\Delta p}{dt}$
1	1.669	1.669	0.223	50	0.562	28.10
3	1.589	4.73	0.201	55	0.532	29.30
5	1.495	7.48	0.174	65	0.451	29.30
7	1.410	9.87	0.149	75	0.391	29.35
9	1.333	12.00	0.124	85	0.340	28.90
11	1.248	13.70	0.097	95	0.293	27.80
13	1.184	15.40	0.072	105	0.262	27.50
15	1.144	17.15	0.058	115	0.233	26.8
17	1.082	18.40	0.035	125	0.206	25.7
20	0.961	19.22	$\bar{1}$.983	135	0.196	26.4
25	0.820	20.50	$\bar{1}$.914	145	0.180	26.1
30	0.758	22.75	$\bar{1}$.880	265	0.0663	17.6
35	0.695	24.32	$\bar{1}$.842	275	0.0609	16.75
40	0.650	26.00	$\bar{1}$.815	343	0.0367	12.6
45	0.603	27.1	$\bar{1}$.780			

As in the uptake of oxygen on water bound film an agreement with the Roginsky-Zeldovich equation was obtained (Fig. 23) in the initial stages:-

$$\log_{10} \frac{d\Delta p}{dt} = b(\Delta p' - \Delta p)$$

Where b and $\Delta p'$ have two sets of values:-

$b = -0.0128$; -0.00634 and b for "dark" uptake $= -0.0759$

$\Delta p' = 25$; 95 divs.

During the later stages of the uptake ($\Delta p > 80$ divs.) an agreement between the rate of pressure decrease and the pressure decrease was found to correspond to:-

$$\frac{d\Delta p}{dt} = K\left(\frac{\Delta_\infty p - \Delta p}{\Delta p}\right) \qquad \text{(Fig. 24)}$$

Where $\Delta_\infty p = 564$ divs. (650 μ moles/gm.)

and $K = -0.062$.

Products: Apart from small amounts of H_2O, N_2O was the only gaseous product detected. The preliminary evacuation products $\Delta_1 H_2O = 3.74\ \mu$. An analysis of the gas phase obtained on reducing the pressure in the reaction vessel/

vessel to ~ 0.1 mm. gave:-

$$\Delta_g N_2O = 9.41\,\mu$$

$$\Delta_g H_2O = 0.24\,\mu$$

Further evacuation of the illuminated film at 10^{-5} mm. for 6 hrs. gave:-

$$\Delta_2 N_2O = 1.07\,\mu$$

$$\Delta_2 H_2O = 4.86\,\mu$$

A further 24 hr. evacuation gave:-

$$\Delta_3 N_2O = 0.29\,\mu$$

$$\Delta_3 H_2O = 2.45\,\mu$$

On extracting the illuminated film with distilled water, treatement with the Griess Llosvay reagent indicated the formation of 13.0 μ NO_2^- (total nitrite).

The observed pressure decrease due to "dark" uptake was 41.0 divs. = 3.02 μ.

The observed pressure decrease due to illumination was 348 divs. = 25.7 μ.

On the assumption that the photoprocess was a "light activated" uptake and chemically identical to the "dark" uptake, the total pressure decrease was:-

$$\Delta p_{total} = 28.7\,\mu.$$

Present in the gas phase was 9.41 μ N_2O and therefore the amount of the nitric oxide uptake was $\Delta NO = \Delta p_{total} + \Delta_g N_2O = 28.7 + 9.41 = 38.1\,\mu$.

The ratio $\Delta NO : \Delta_g N_2O = 38.1 : 9.41$

$$= 1.00 : 0.247$$

i.e. N_2O was produced in the gas phase in an amount equal to 25% of the uptake of NO and this confirms the observations made by Kennedy (13) that on illumination the overall process was:-

$$\underset{\text{gas}}{4NO} \xrightarrow[\text{tit. diox.}]{\lambda < 4000} \underset{\text{adsorbed}}{N_2O_3} + \underset{\text{gas}}{N_2O} \qquad (1)$$

when/

when based on pressure measurements alone. On degassing the film at 25°C, however, further quantities of N_2O were evolved, presumably on slow diffusion from the interior of the film in a manner similar to that observed with carbon dioxide from illumination in oxygen of acetone bound films. The total amount of N_2O evolved on degassing was:-

$$\Delta_g N_2O + \Delta_2 N_2O + \Delta_3 N_2O = 10.78\,\mu$$

The total nitrite produced was 13.0 μ and it seemed possible that the ultimate amount of N_2O produced on degassing would also have been 13.0 μ in order to conform to the equation:-

$$3NO \xrightarrow[\text{tit. diox.}]{\lambda < 4000\text{Å}} N_2O + NO_2^- \qquad (2)$$

as is found to occur between zinc oxide "hyperfine" and nitric oxide on illumination (19). In support of this equation the total uptake of nitric oxide was 28.7 μ and the ratio:-

$$\Delta NO : \Delta N_2O : \Delta NO_2^- = 38.1 : 10.8 : 13.0$$
$$\approx 3.00 : 0.85 : 1.02$$

is in reasonably good agreement with equation 2 with a low yield of N_2O (85%) due to diffusion restrictions or a slow decomposition of a surface sorbed product. The ease with which the nitrite was extracted with water in a quantitative yield would be in accordance with a weak surface bonding. Small amounts of water were produced photochemically but not in sufficient quantities to be considered as a major product. An approximate estimate of the amount produced would be $\Delta H_2O \approx 3\,\mu$.

The extrapolated value of $\Delta_\infty p$ was 564 divs. and taking this into account with the dark uptake, $\Delta_\infty p_{total}$ = 605 divs. equivalent to 704 μ/gm. Since this uptake would occur after an infinite time of illumination it is reasonable to postulate/

postulate that all N_2O produced will have had time to diffuse into the gas phase with the result that $\Delta p_{total} = 2/3 \Delta NO$. The theoretical extrapolated nitric oxide uptake based on equation 2 is then:-

$$\Delta NO = 1056\mu/gm.$$

In comparison with the oxygen uptake on films 2,3,4,5,6 and 7 (p61) the value $\Delta NO = 1056\mu/gm.$ would indicate 6 NO molecules reacting to give $2N_2O$ and $2NO_2^-$ - on 176 (i.e. $\frac{1056}{6}$) μ mole sites /gm. This corresponds favourably with the values 176 (film 2); 179 (film 3); 171 (films 4,5,6) and 171 (film 7).

Summary of nitric oxide uptake

(1) Contact between nitric oxide and titanium dioxide resulted in a chemisorption of the nitric oxide in agreement with the Roginsky-Zeldovitch equation:-

$$\log \frac{d\Delta p}{dt} = b(\Delta p' - \Delta p).$$

The rate of chemisorption decayed rapidly.

(2) On illumination nitric oxide was rapidly removed from the gas phase. The kinetics of the pressure decrease were similar to that of the oxygen pressure decrease over a water bound film; both were initially in agreement with the Roginsky-Zeldovitch equation. Again, as for oxygen, in the later stages of the process an excellent agreement was found with the equation:-

$$\frac{d\Delta p}{dt} = K\left(\frac{\Delta p - \Delta p}{\Delta p}\right).$$

(3) Nitrous oxide was a major product occurring from the reaction:-

$$3NO \xrightarrow{\lambda < 4000\text{Å}} N_2O + NO_2^-.$$

The /

The yeild of N_2O and NO_2^-, based on the nitric oxide uptake were respectively 85% and 102%.

(4) In order to balance equation 2 an electron is required:-

$$3NO + e \longrightarrow N_2O + NO_2^- \qquad (3)$$

confirming the n-type character of the titanium dioxide.

(5) The ease of extraction of NO_2^- in quantitative yield indicated a surface process on the titanium dioxide.

(6) The extrapolated value of $\Delta_\infty NO$ was in accordance with a process of :-

$$6NO + 2e \longrightarrow 2N_2O + 2NO_2^-$$

occurring on 176 μ mole unit sites/gm. titanium dioxide. Thus correlating the nitric oxide uptake to the uptake of oxygen;- see summary on films 2, 3, 4, 5, 6, and 7. (p.61).

TITANIUM DIOXIDE AND AMMONIA

The photo-reaction between titanium dioxide and ammonia has already been investigated in aqueous phase by Gopalarao (39), and Gopalarao and Murty (40). Exposure of an air containing suspension of titania gel (colloided) in dilute ammonia solution to light of $\lambda < 4000\text{Å}$ resulted in the oxidation of ammonia to nitrite and the equation (39) suggested was:-

$$3TiO_2.NH_3 + h\nu \longrightarrow 3TiO_2.NH_3^{\boxtimes} \longrightarrow 3TiO + H_2O + HNO_2$$

with the adsorbed layer of ammonia acting as the seat of the light absorption.

Further work (40) on the oxidation of ammonia in aqueous media showed the photo process to be subject to the following conditions:-

(1) An 800% change in the concentration of ammonia resulted in only a 16% change of rate in nitrite production thereby suggesting a zero order reaction.

(2) The nitrite concentration increased proportionately with the time before tending towards a maximum. This again suggests a zero order reaction.

(3) The rate of reaction increased, at first, proportionately to the amount of titanium dioxide and then tended to reach a maxiumum, indicating that the titanium dioxide acted as a photo-sensitiser and may have taken a definite part in the reaction:-

$$\text{(a)}\quad 6TiO_2^{\boxtimes} + \text{light} \longrightarrow 6TiO_2^{\circledcirc},$$

$$\text{(b)}\quad 6TiO_2^{\boxtimes} + NH_3 \longrightarrow 3Ti_2O_3 + H_2O + HNO_2,$$

$$\text{(c)}\quad Ti_2O_3 + \tfrac{1}{2}O_2 \longrightarrow 2TiO_2.$$

(4) The rate of reaction was found to depend upon the Ph of the solution. The optimum value was Ph = 9, i.e. the reaction proceeded faster in the presence of hydroxyl ions. Again the nitrite concentration was observed /

observed to reach a maximum.

(5) The photo-process was retarded by the presence of foregin ions with the effect:- $Na^{+} < Ba^{++} < Al^{+++}$. i.e. in order of coagulating efficiency of colloidal suspensions.

(6) Variation of the wavelength of light used caused a variation in the relative yield of nitrite. High yields of nitrite were obtained from $\lambda < 4050\text{Å}$.

The experiments of Gopalarao and Murty were performed on colloidal suspensions of titanium dioxide in dilute ammonia solutions contained in a glass stoppered quartz vessel. It is immediately apparent that the limiting concentrations of nitrite observed on illumination could be attributed to the limited amount of dissolved oxygen, and that the titanium dioxide plays only an intermediate role. This they have indicated in equations a,b and c, the oxidation taking place in an adsorbed layer of ammonia molecules.

SORPTION OF AMMONIA ON TITANIUM DIOXIDE.

A known quantity (0.1 g.) of titanium dioxide was accurately weighed out into a clean dry reaction flask and evacuated in the usual way. When a known quantity of ammonia was introduced into the evacuation reaction vessel the resultant ammonia pressure in equilibrium with the titanium dioxide was in accordance with considerable adsorption.

Film 9

Wt. Sample II	0.1026 gms. (wt. after evacuation)
Total reaction volume	111.2 mls.

The amount of ammonia adsorbed was large. Desorption of the ammonia for 24 hours at 25°C preceded a second similar sorption with the same quantity of /

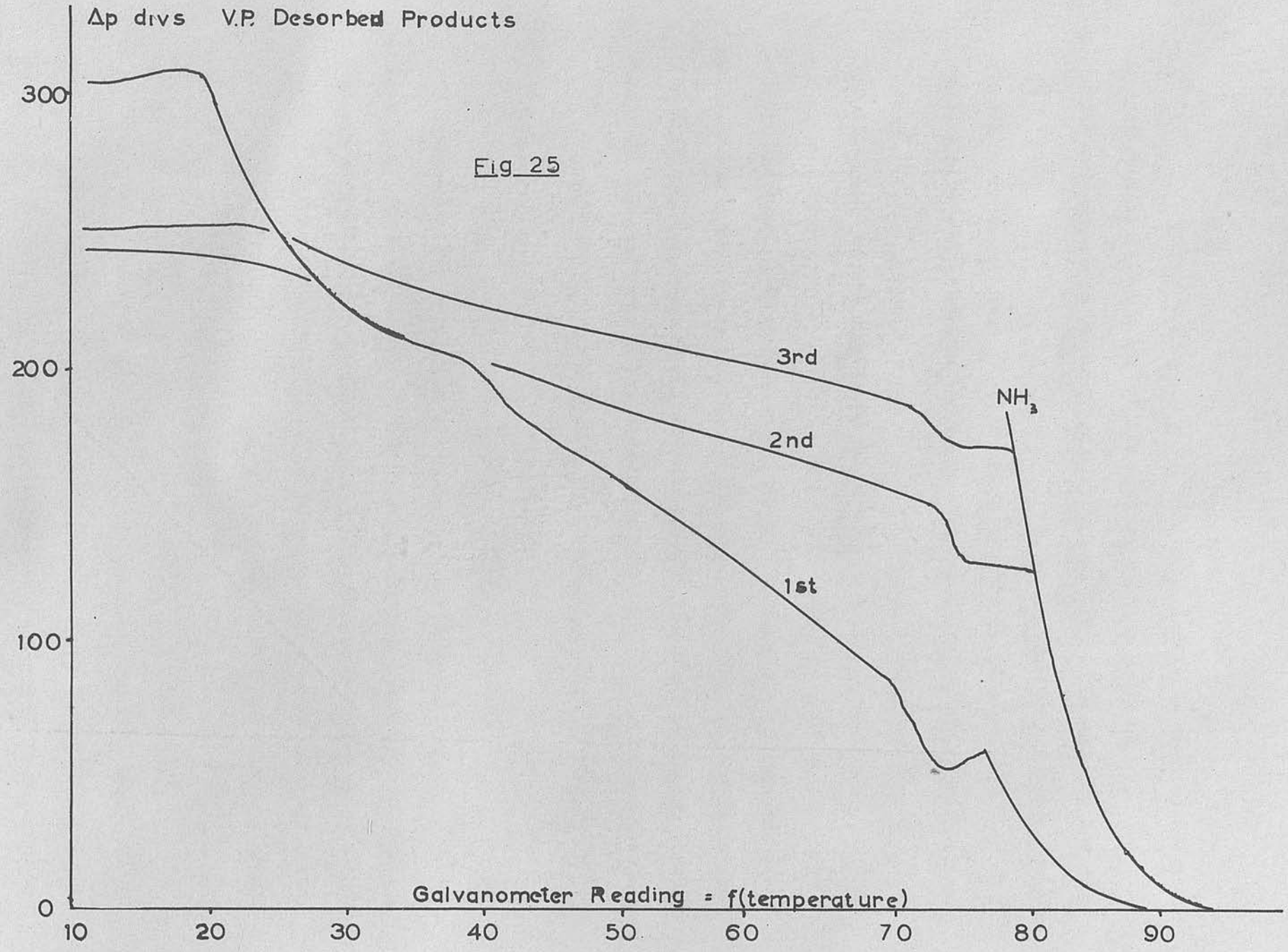
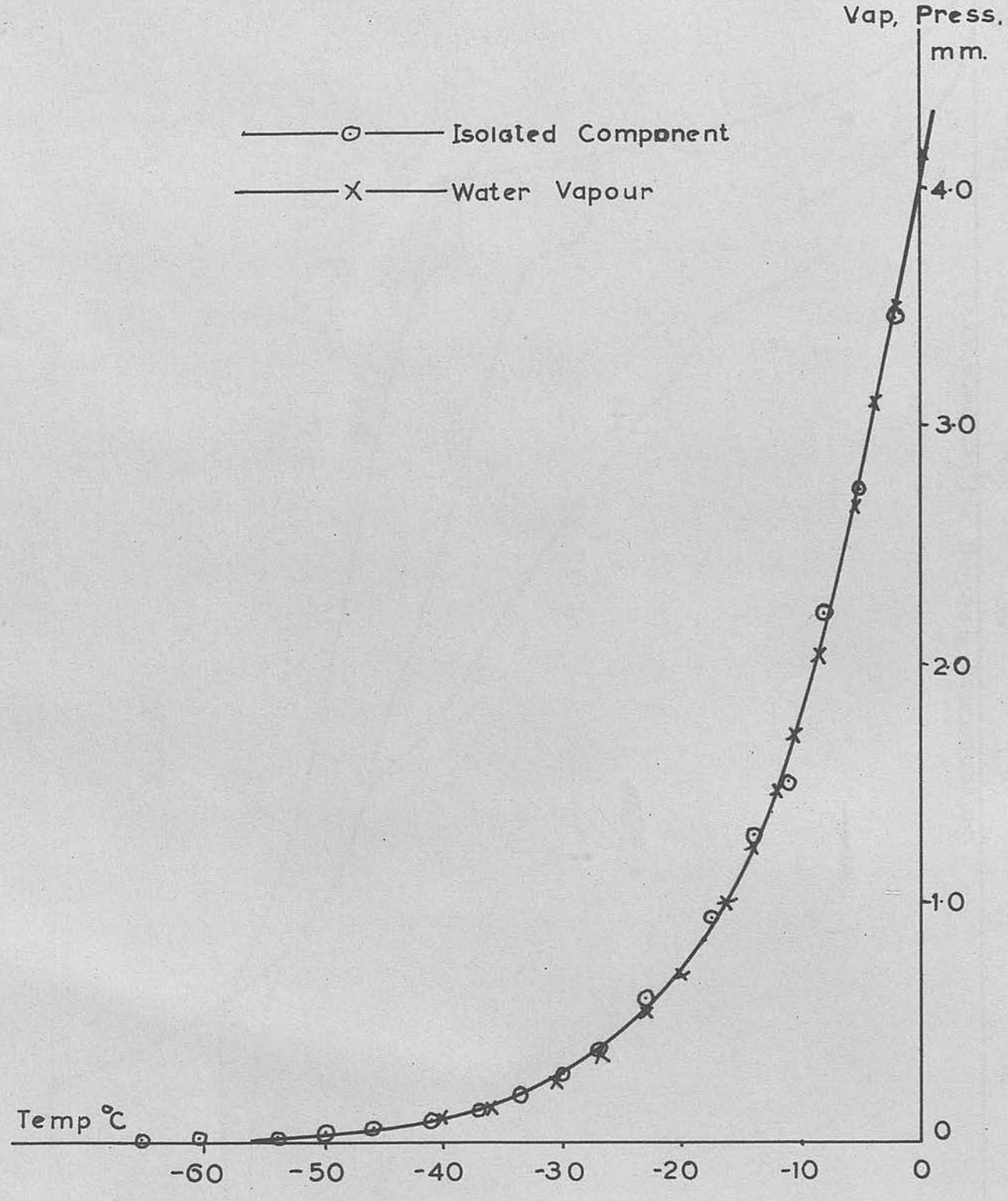

Δp dıvs V.P. Desorbed Products
300
200
100
0
3rd
2nd
1st
NH3
Galvanometer Reading = f(temperature)
10
20
30
40
50
60
70
80
90

Fig 25

Fig 26


Vap, Press.
mm.
Isolated Component
Water Vapour
4·0
3·0
2·0
1·0
0
Temp °C
-60
-50
-40
-30
-20
-10
0

of ammonia. This time the extent of the sorption was smaller. When repeated a third time the sorption was slightly less than the second.

Table XXIV

	1st sorption	2nd sorption	3rd sorption
Total ammonia in 111·2 mls. μ	459	462	456
Theoretical ammonia pressure mm.	73·6	74·1	73·1
Measured ammonia pressure mm.	54·1	60·4	59·8
Amount of ammonia sorbed μ	129	94	92
Amount of ammonia sorbed%	28·6	20·4	20·2

A decreasing sorptive capacity for ammonia is illustrated in Table XXIV.

A rough physical analysis by the simple method on the desorbed ammonia showed the presence of two components. This is illustrated in Fig. 25. It was evident that the ammonia content of the desorbed products increased with each desorption. By repeatedly passing the first desorption products through a cold trap at - 80°C a second less volatile component was isolated. Measurements of the vapour pressure of the isolated component at varying temperatures (see Table XXV) are plotted in Fig. 26. The curve is superimposed upon the plots obtained for pure water vapour degassed by low pressure distillation.

Table XXV

Isolated Component				Water Vapour			
Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
-69.3	0.00	-30.0	0.288	-64.0	0.05	-14.0	1.25
-65.3	0.014	-27.0	0.385	-59.0	0.08	-12.0	1.47
-60.5	0.020	-23.0	0.603	-40.0	0.10	-10.5	1.71
-54.0	0.025	-17.5	0.945	-36.0	0.14	- 8.5	2.04
-50.0	0.041	-14.0	1.289	-30.5	0.25	- 5.3	2.67
-45.9	0.059	-11.2	1.517	-26.9	0.37	-33.7	3.10
-41.1	0.091	- 8.0	2.220	-23.0	0.54	- 2.0	3.50
-37.0	0.136	- 5.0	2.735	-20.0	0.70	+ 0.4	4.15
-33.6	0.202	- 2.0	3.460	-16.3	1.00		

From /

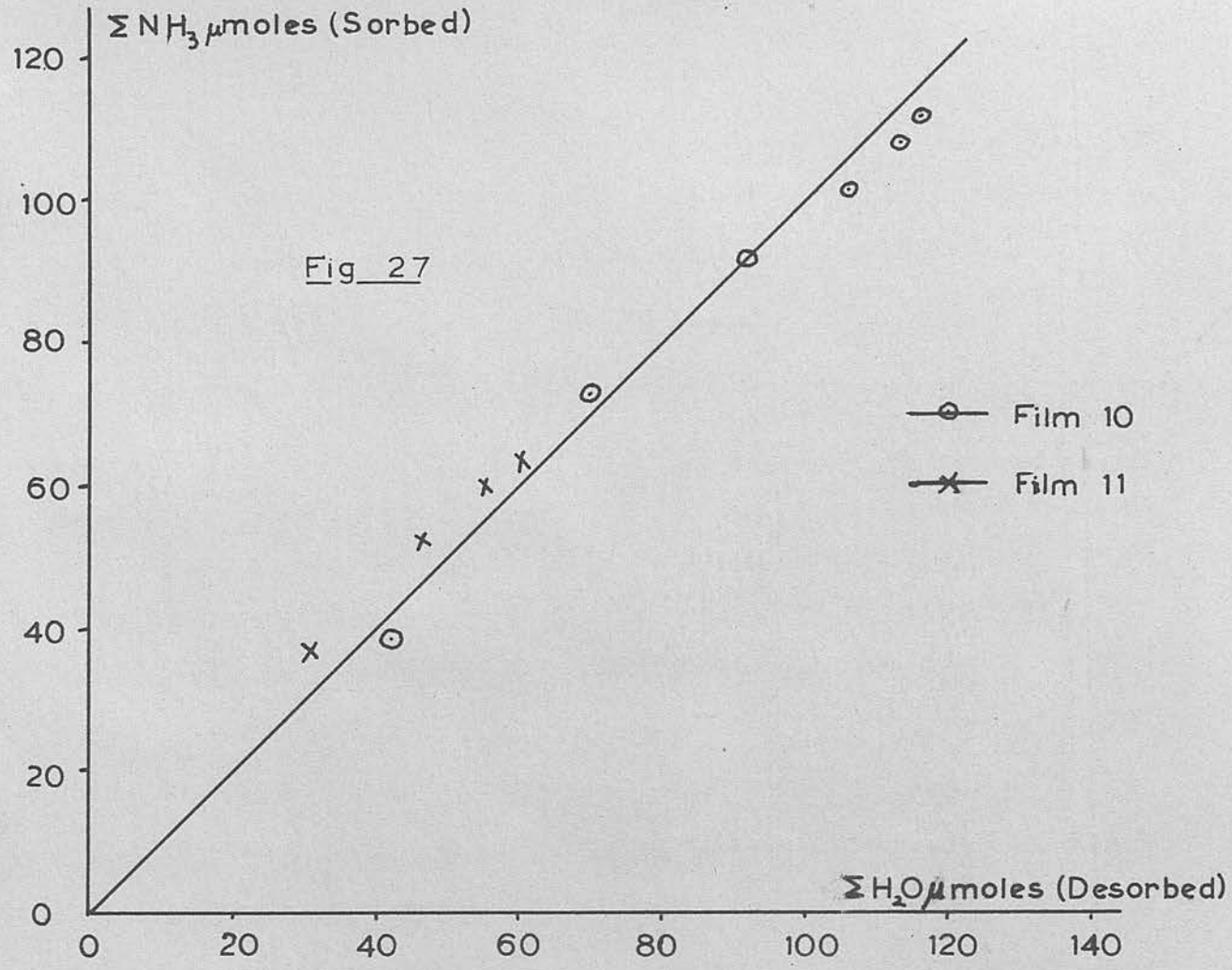

Σ NH3 μmoles (Sorbed)
120
100
80
60
40
20
0
Film 10
Film 11
Σ H2O μmoles (Desorbed)
0
20
40
60
80
100
120
140

Fig 27

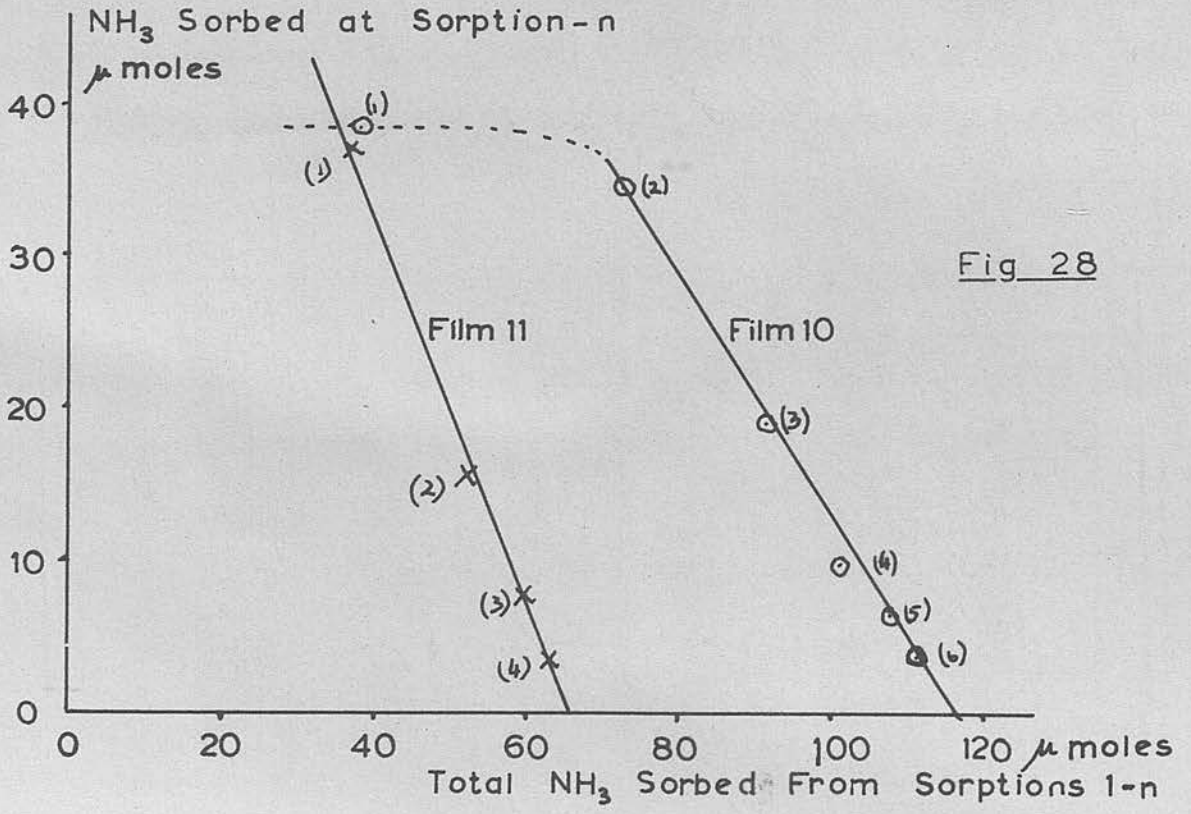

NH3 Sorbed at Sorption-n
μ moles
40
30
20
10
0
(1)
(2)
(3)
(4)
(5)
(6)
Film 11
Film 10
0
20
40
60
80
100
120 μ moles
Total NH3 Sorbed From Sorptions 1-n

Fig 28

From Fig. 26 there can be no doubt that the isolated component was water.

Having thus established the presence of appreciably large amounts of water occurring in desorbed ammonia, attempts were then made successfully to measure the amount desorbed.

CHEMISORPTION OF AMMONIA ON TITANIUM DIOXIDE

Accurately measured quantities of ammonia ($\sim 45\ \mu$) were sorbed on to films 10 and 11. Each sorption was allowed to reach equilibrium, after 24 hours, (25°C) and the same time period allowed for desorption (25°C) by condensation in vacuo into a trap at liquid oxygen temperatures. In all, six ammonia sorptions and desorptions were analysed for film 10 and four for film 11. The quantity of ammonia admitted during each sorption was such that it gave initially a pressure of 6.0 mm. in the system used for analysis. A time interval of twelve months elapsed between the measurements on films 10 and 11.

Film 10.

Wt. Sample II 0.1763 gms. (wt. after evacuation)

Reaction volume 150 mls.

Ammonia gas pressure ~ 0.3 mm. after sorption

Analytical results of six sorptions and desorptions are given in Table XXVI.

Table XXVI

Sorption	Initial	Desorbed Products		Sorbed	Total Process		Total Products.
n	NH_3 μ	NH_3 μ	H_2O μ	NH_3 μ	ΣNH_3 sorbed μ	ΣH_2O desorbed μ	μ
1	44.4	6.1	42.1	38.3	38.3	42.1	48.2
2	44.4	10.0	27.0	34.4	72.7	69.9	37.0
3	44.0	25.1	21.8	18.9	91.6	91.7	46.9
4	44.1	34.4	14.5	9.7	101.3	106.2	48.9
5	43.7	37.3	7.3	6.4	107.7	113.5	44.6
6	44.1	40.4	2.6	3.7	111.4	116.1	43.0

Total initial ammonia 264.7 μ

Total products(ammonia + water) 268.6 μ

Film 11 /

Film 11.

Wt. Sample II 0.1027 gms. (wt. after evacuation)

Reaction Volume 33.9 mls.

Ammonia gas pressure ~1.0 mm. after sorption.

Table XXVII

Sorption	Initial	Desorbed Products		Sorbed	Total Process		Total Products Desorbed $NH_3 + H_2O$
n	NH_3	NH_3	H_2O	NH_3	ΣNH_3 sorbed	ΣH_2O desorbed	
	μ	μ	μ	μ	μ	μ	μ
1	45.9	9.3	31.0	36.8	36.8	31.0	40.3
2	43.1	27.6	15.5	15.5	52.3	46.5	43.1
3	45.8	38.2	8.8	7.6	59.9	55.3	47.0
4	42.9	39.6	9.2	3.3	63.2	60.5	44.8

Total initial ammonia 137.7 μ

Total products (ammonia + water) 135.2 μ

For both films the amount of products obtained on desorption was the same (in molecules) as the amount of ammonia admitted for sorption. This indicated a one to one ratio of displacement of water by ammonia. In Fig. 27 the stepwise increase in the ammonia sorbed is plotted against the stepwise increase of the water desorbed. A reasonably good agreement is obtained with the theoretical continuous line for a one to one displacement of water by ammonia.

Fig. 28 illustrates the empirical linear relationship that existed between the amount of ammonia that was sorbed during a particular sorption n and the total amount of ammonia that had been sorbed during sorptions 1, 2 .....n. Extrapolation of the linear plot to the extreme case when no ammonia would be sorbed (after ∞ sorptions) gave the ultimate thermal ammonia uptake.

For films 10 and 11 the limiting values of the ammonia uptake were respectively /

respectively 116μ and 65. 7 μ

Film 10 Ammonia uptake = 658 μ/gm.
Film 11 Ammonia uptake = 640. μ/gm.

Average Amonnia uptake = 650 μ/gm.

The ammonia sorbed in this manner was not degassed by evacuation: hence the term "chemisorption."

It is now becoming apparent that there was a common factor of 170 μ/gm. connecting all the processes so far examined. Very possibly 170 μ/gm. was a measure of surface "impurity centres" and that the integer preceding this value (4 in the case of $NH_3 \rightarrow H_2O$) was the number of molecules which associated with each impurity centre.

REVERSIBILITY OF AMMONIA UPTAKE.

Measured quantities of water vapour were admitted to a film of 0.0704 gms. Sample II (wt. after evacuation) which had been treated with ammonia as in films 10 and 11. (Ammonia sorbed = 650 x .0704 = 45.7 μ). Admission and desorption of 36.7 μ water vapour produced only 2.7 μ NH_3. A second admission and desorption of 61.9 μ water produced a further 3.7 μ NH_3. Although the recovery was only 14% of the adsorbed ammonia, the process is regarded as reversible.

$$\underset{\text{chemisorbed}}{(H_2O)} + \underset{\text{adsorbed}}{NH_3} \rightleftharpoons \underset{\text{chemisorbed}}{(NH_3)} + \underset{\text{adsorbed}}{H_2O}$$

In the presence of excess ammonia the equilibrium state would be in favour of chemisorbed ammonia.

KINETICS OF AMMONIA SORPTION

The pressure changes accompanying the sorption of ammonia on titanium dioxide were noted in relation to time and Table XXIX gives an analysis of derived /

derived rate curves. The pressure in the reaction system was regarded as due to ammonia alone for reasons that will become apparent in the discussion. The rate of pressure decrease of ammonia was found to be two laws:-

(1) When the ambient ammonia pressure was greater than 1.0 mm. an agreement was found with the Roginsky-Zeldovitch equation for chemisorption (Fig. 29 numerals indicating the sorption in question).

(2) At ammonia pressures below 0.2 mm. the rate of pressure decrease was found to vary with $p^2_{NH_3}$ (Fig.30). Between 0.2 and 1.0 mm. an indefinite relation existed.

Further data referring to the conditions of Table XXIX are given in Table XXVIII.

Table XXVIII

Graph	Sample II gms.	Place in sorption series on films.	Volume of System mls.	Initial Ammonia μ
1	0.0768	3rd	66	32.4
2	0.0768	2nd	66	22.9
3	0.0768	1st	66	32.4
4	Film 11	2nd	73	43.1
5	Film 11	1st	73	45.9
6	Film 10	3rd	190	44.0

Table XXIX /

Figs 29 & 30

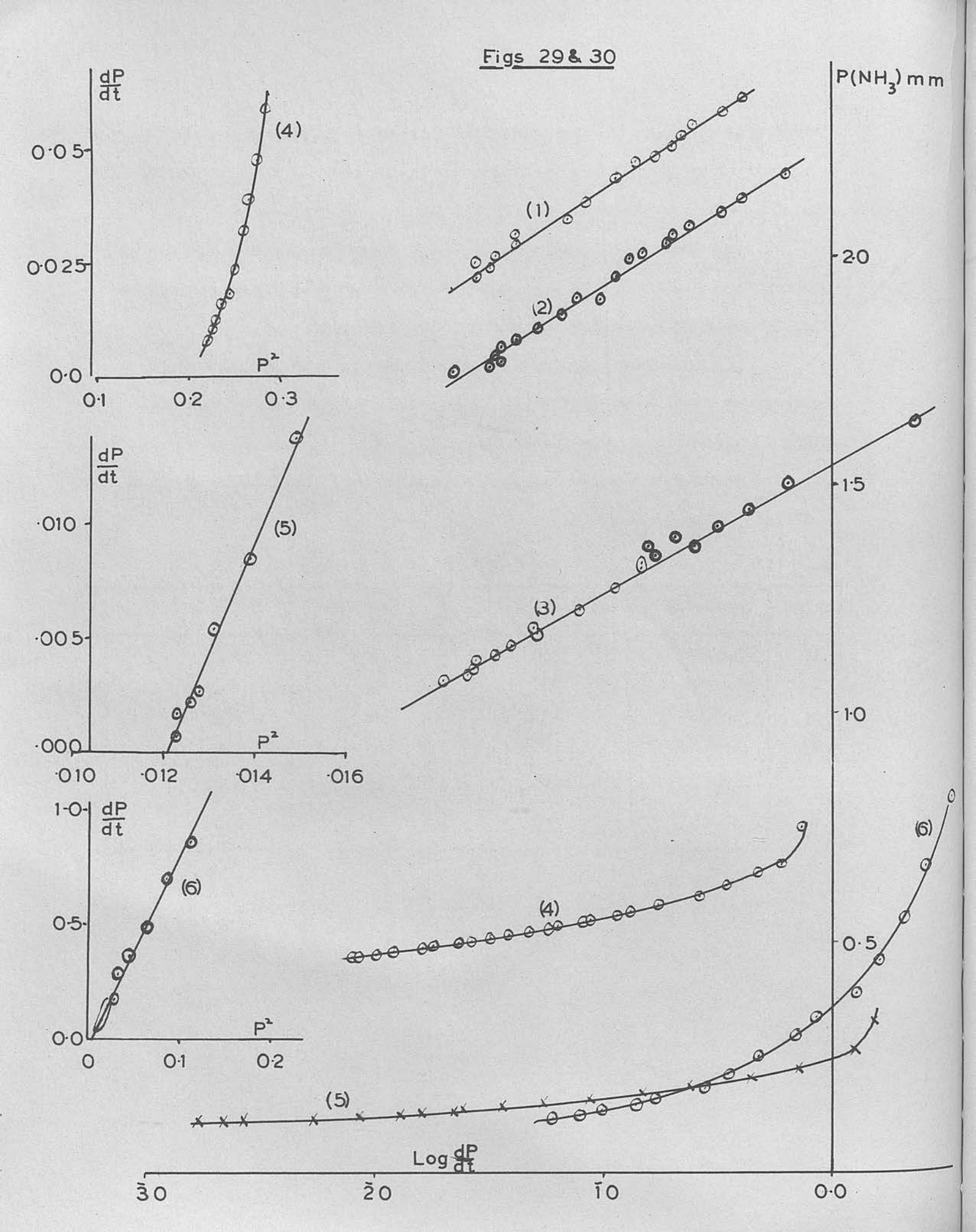

dP/dt
0·05
0·025
0·0
(4)
P²
0·1
0·2
0·3
dP/dt
·010
·005
·000
(5)
P²
·010
·012
·014
·016
1·0
dP/dt
0·5
0·0
(6)
P²
0
0·1
0·2
P(NH3) mm
(1)
(2)
2·0
(3)
1·5
1·0
(4)
(6)
0·5
(5)
Log dP/dt
3̄0
2̄0
1̄0
0·0

Table XXIX ($R = \frac{dp}{dt}$ mm./min.)

1		2		3		4			
P_{NH_3}	Log R	Pmm	Log R	P	Log R	P	R	Log R	P^2
2.40	$\bar{1}$.881	2.180	$\bar{1}$.806	1.641	0.371	.750	.749	$\bar{1}$.875	.562
2.35	1.611	2.130	$\bar{1}$.613	1.503	1.811	.673	.619	1.787	.452
2.32	$\bar{1}$.533	2.097	$\bar{1}$.519	1.446	$\bar{1}$.642	.653	.482	$\bar{1}$.683	.427
2.29	1.388	2.070	1.280	1.410	1.507	.625	.357	1.553	.391
2.265	$\bar{1}$.343	2.047	1.310	1.384	1.321	.600	.268	$\bar{1}$.428	.360
2.243	$\bar{1}$.300	2.029	$\bar{1}$.180	1.363	1.402	.481	.178	$\bar{1}$.250	.229
2.222	$\bar{1}$.233	2.010	$\bar{1}$.175	1.363	$\bar{1}$.302	.569	.134	$\bar{1}$.127	.324
2.208	$\bar{1}$.144	1.996	$\bar{1}$.114	1.346	$\bar{1}$.233	.559	.104	$\bar{1}$.070	.313
2.122	2.933	1.910	$\bar{2}$.989	1.319	$\bar{1}$.176	.544	.0830	$\bar{2}$.919	.296
2.122	$\bar{1}$.056	1.956	$\bar{1}$.057	1.330	$\bar{1}$.176	.551	.0882	$\bar{2}$.946	.304
2.083	$\bar{2}$.843	1.910	2.891	1.257	$\bar{1}$.063	.538	.0641	$\bar{2}$.808	.290
2.052	$\bar{2}$.617	1.875	$\bar{2}$.820	1.227	$\bar{2}$.903	.533	.0588	$\bar{2}$.769	.285
2.030	$\bar{2}$.617	1.844	$\bar{2}$.717	1.187	$\bar{2}$.688	.525	.0479	$\bar{2}$.680	.276
2.006	$\bar{2}$.532	1.822	$\bar{2}$.622	1.170	$\bar{2}$.717	.516	.0390	$\bar{2}$.591	.267
1.991	$\bar{2}$.442	1.804	$\bar{2}$.555	1.149	$\bar{2}$.602	.510	.0322	$\bar{2}$.508	.260
1.976	$\bar{2}$.505	1.787	$\bar{2}$.531	1.627	$\bar{2}$.503	.501	.0236	$\bar{2}$.373	.251
1.958	2.448	1.771	$\bar{2}$.555	1.110	$\bar{2}$.447	.492	.0182	$\bar{2}$.260	.246
		1.759	$\bar{2}$.505	1.097	$\bar{2}$.440	.485	.0161	$\bar{2}$.207	.236
		1.754	$\bar{2}$.341	1.086	$\bar{2}$.413	.479	.0123	$\bar{2}$.090	.229
				1.072	$\bar{2}$.301	.475	.0102	$\bar{2}$.009	.226
						.471	.0080	$\bar{3}$.90	.222
						.468	.0085	$\bar{3}$.93	.219

5				6			
P_{NH_3} mm	R mm/min	Log R	P^2	P	R	Log R	P^2
0.325	1.51	0.179	0.1060	0.818	3.78	0.58	0.679
0.265	1.23	0.090	0.0702	0.665	2.66	0.43	0.443
0.225	.712	$\bar{1}$.853	0.0507	0.551	2.02	0.31	0.304
0.205	.439	$\bar{1}$.643	0.0420	0.461	1.62	0.21	0.213
0.187	.238	$\bar{1}$.377	0.0350	0.388	1.28	0.11	0.151
0.170	.149	$\bar{1}$.137	0.0290	0.336	0.86	$\bar{1}$.94	0.113
0.158	.0876	$\bar{2}$.943	0.0253	0.287	0.70	$\bar{1}$.95	0.0860
0.150	.0552	$\bar{2}$.742	0.0225	0.253	0.48	$\bar{1}$.68	0.0640
0.143	.0372	$\bar{2}$.571	0.0205	0.214	0.36	$\bar{1}$.56	0.0460
0.132	.0222	$\bar{2}$.352	0.0172	0.158	0.17	$\bar{1}$.23	0.0280
0.127	.0161	$\bar{2}$.207	0.0161	0.146	0.14	$\bar{1}$.15	0.0214
0.122	.0129	$\bar{2}$.111	0.0149	0.135	0.10	$\bar{1}$.00	0.0181
01118	.0085	$\bar{2}$.93	0.0139	0.123	0.08	2.90	0.0151
0.115	.0054	$\bar{3}$.73	0.0131	0.116	0.06	$\bar{2}$.78	0.0132
0.113	.0027	$\bar{3}$.43	0.0128				
0.112	.0022	$\bar{3}$.34	0.0126				
0.111	.0017	$\bar{3}$.23	0.0123				
0.11	.0007	$\bar{4}$.83	0.0123				

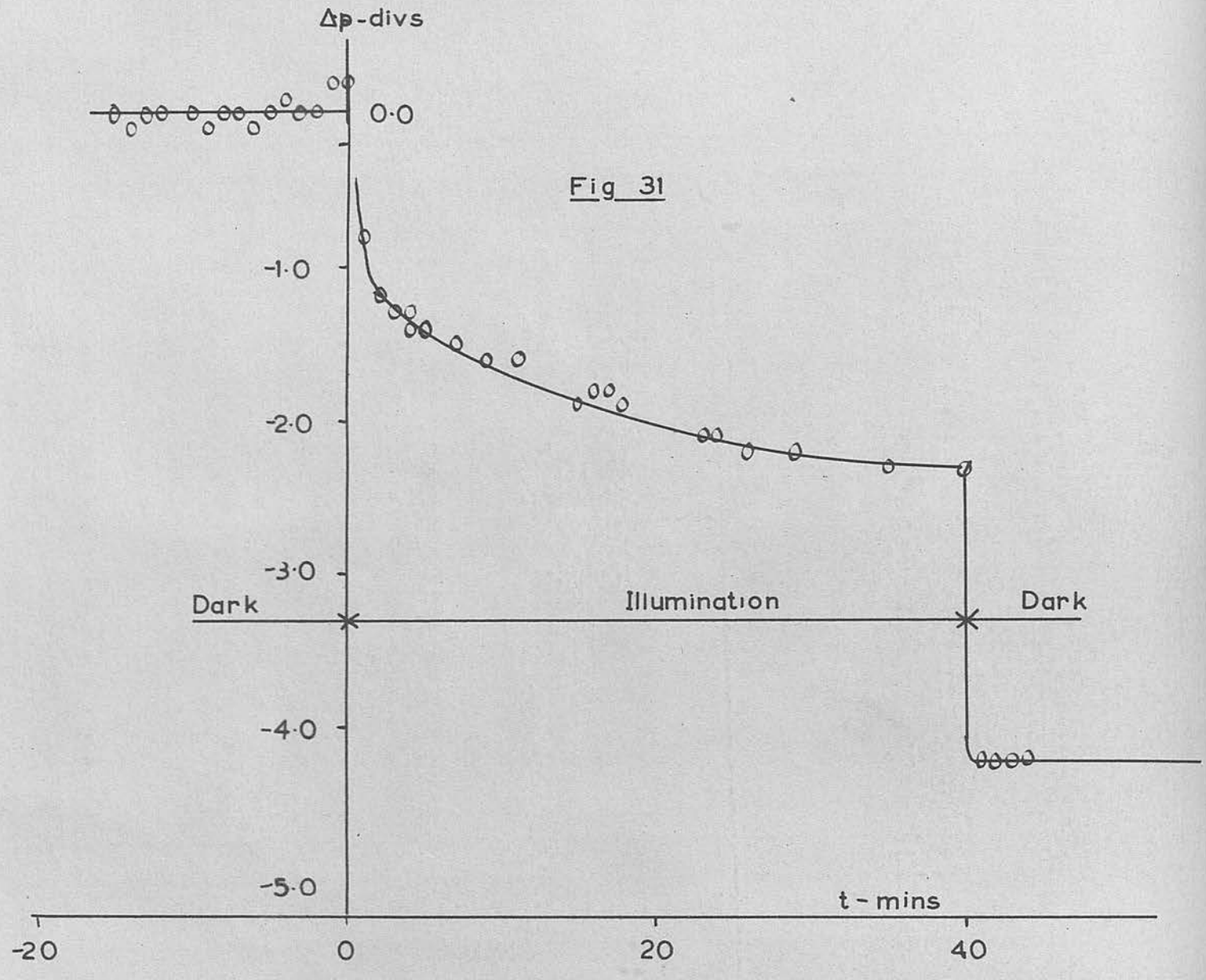

Δp-divs
0·0
-1·0
-2·0
-3·0
-4·0
-5·0
Dark
Illumination
Dark
t-mins
-20
0
20
40

Fig 31

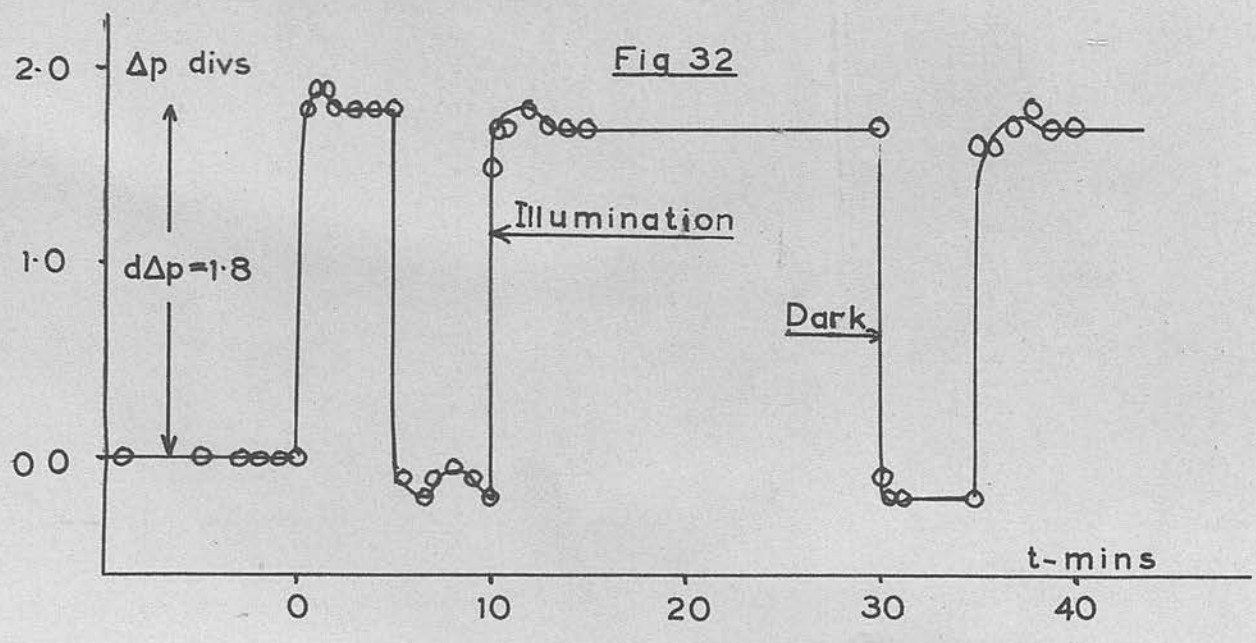

2·0
Δp divs
1·0
dΔp=1·8
0 0
Illumination
Dark
t-mins
0
10
20
30
40

Fig 32

PHOTO-OXIDATION OF CHEMISORBED AMMONIA.

Attempts to show a definite photochemical oxidation of ammonia (in the absence of gaseous oxygen) on illuminated titanium dioxide proved unsuccessful. There was, however, a photo effect upon the ambient ammonia pressure as was illustrated by film 12. The water displacement reaction had already been completed.

Film 12.

Wt. Sample II 0.0989 gms. (wt. after evacuation)

Reaction Volume 28.6 mls.

Ammonia pretreatment 64.2 μ (complete)

Theoretical ammonia pressure (no sorption) 43.0 mm.

Measured ammonia pressure (equilibrium) 8.3 mm.

Gauge sensitivity 0.0230 mm./divs.

The effect of illumination on the above system is given in Table XXX in the usual symbols Δp and t.

Table XXX

t	Δp	t	Δp	t	Δp	t	Δp
.0[⊠]	0	9	1.8	23	2.3	41	4.4
1	1.0	11	1.8	24	2.3	42	4.4
2	1.4	15	2.1	26	2.4	43	4.4
4	1.5	16	2.0	29	2.4	60	4.4
5	1.6	17	2.0	35	2.5		
7	1.7	18	2.1	40[I]	2.5		

[⊠] Illumination commenced

[I] Illumination discontinued.

A /

A very small pressure decrease (2.5 divs) occurred on illumination (see Fig.31). Discontinuation of the illumination was accompanied by an instantaneous pressure decrease of 1.9 divs. As in Fig. 32, an instantaneous pressure increase resulted on subsequent re-illumination.

A similar phenomenon has been observed by Rosenberg and Martel (41) on the illumination of adsorbed krypton on germanium, graphite and titanium dioxide which, they say, was due to a heating effect caused by the adsorption of light by the adsorbent. Such an effect on the ammonia-titanium dioxide system would require an increase in temperature of the adsorbent probably of the order of 0.05 to 0.10°C.

Illumination of the thermally ammonia treated titanium dioxide and ammonia results in a very small ammonia uptake (Δp_{NH_3} = 1.5 μ/gm). The illumination may have caused a small increase of temperature of the film (0.05 to 0.10°C).

UPTAKE OF OXYGEN ON AN AMMONIA TREATED FILM.

After determining the thermal ammonia uptake of film 11 a further two saturations with ammonia were considered to have completed the water displacement reaction. After desorption of all excess ammonia, oxygen was admitted to 50 mm. and the film was illuminated. No "dark" uptake of oxygen was observed. The pressure decrease (Δp) on illumination was noted in relation to time (t. mins.) and is given gelow in Table XXXI.

Film 11.

Wt. Sample II	0.1027 (wt. after evacuation)
Reaction Volume	33.9 mls.
Ammonia pretreatment	65.7 μ
Initial oxygen pressure	48.4 mm.
Gauge sensitivity	0.0230 mm./div.

Table XXXI./

Table XXXI

t	Δp	t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	31	36.4	87	70.4	697	256.6	2893	577.9
1	3.1	34	38.7	92	73.2	205	258.3	1950	584.4
2	5.5	37	40.85	97	76.4	718	259.7	3036	594.4
3	7.6	38	41.9	103	78.3	727	763.0	3060	596.9
4	9.1	43	44.9	108	80.4	731	263.9	3191	611.6
5	10.7	46	46.9	114	83.35	736	265.2	3147	617.3
6	12.0	47	47.6	124	87.5	741	266.3	3209	623.7
7	13.7	48	48.2	144	95.4	745	167.3	3244	627.4
8	14.8	48	48.6	163	103.6	749	267.7	4296	717.3
9	16.0	51	50.0	179	110.3	758	269.7	4329	719.6
10	17.0	54	52.3	207	120.5	770	271.0	4371	723.3
12	19.7	57	53.6	224	126.3	813	280.6	4421	726.1
14	21.5	59	54.4	255	137.0	1440	387.2	4463	729.9
16	23.9	63	57.3	264	140.0	1480	393.2	4514	734.5
17	24.0	65	58.4	274	143.4	1509	398.2	4611	742.7
18	24.9	67	59.5	282	146.2	1583	410.8	4652	746.5
20	27.1	71	62.2	290	148.5	1626	418.1	4680	748.4
22	29.0	73	63.1	335	163.2	1686	424.7	4740	753.3
23	29.9	76	64.6	362	170.7	1762	436.9		
26	32.5	78	65.9	402	182.4	1823	444.2		
29	34.8	81	67.4	458	197.6	1903	454.9		

Derived rate values from Table XXXI are given in Table XXXII and shown on Fig. 33.

Table XXXII /

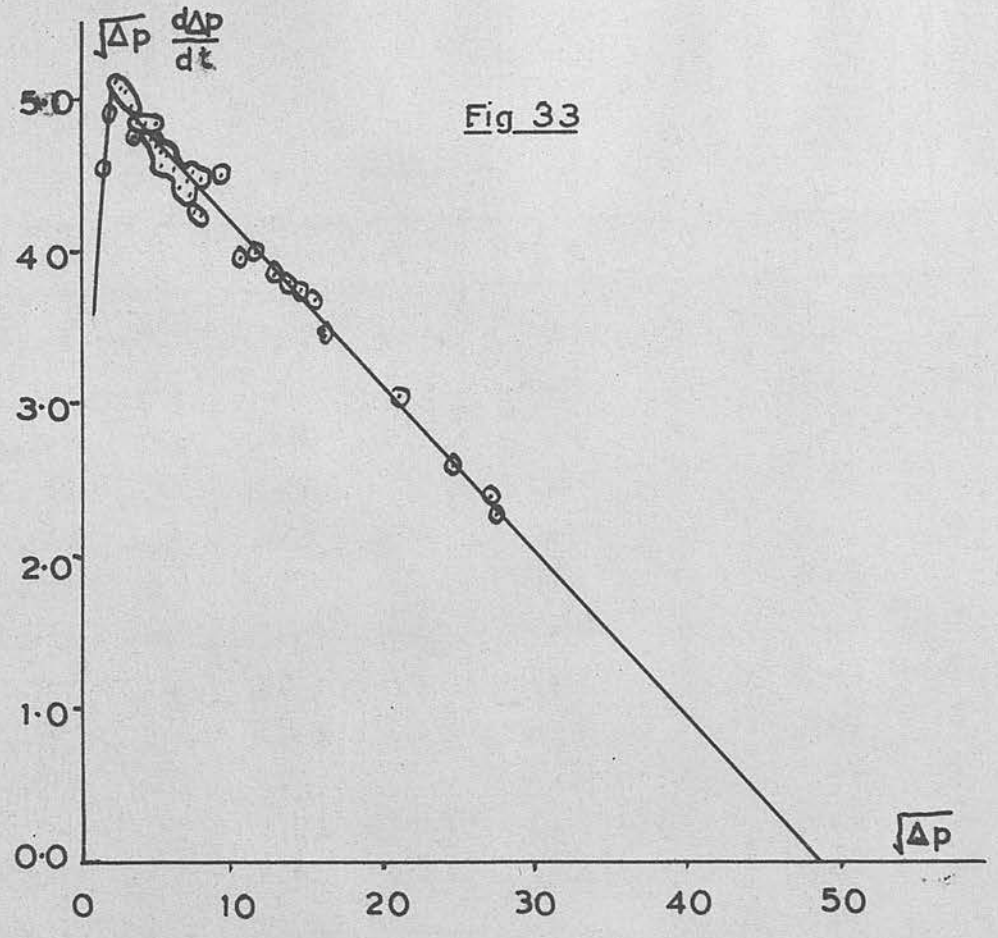

√Δp dΔp/dt
5·0
4·0
3·0
2·0
1·0
0·0
0
10
20
30
40
50
√Δp

Fig 33

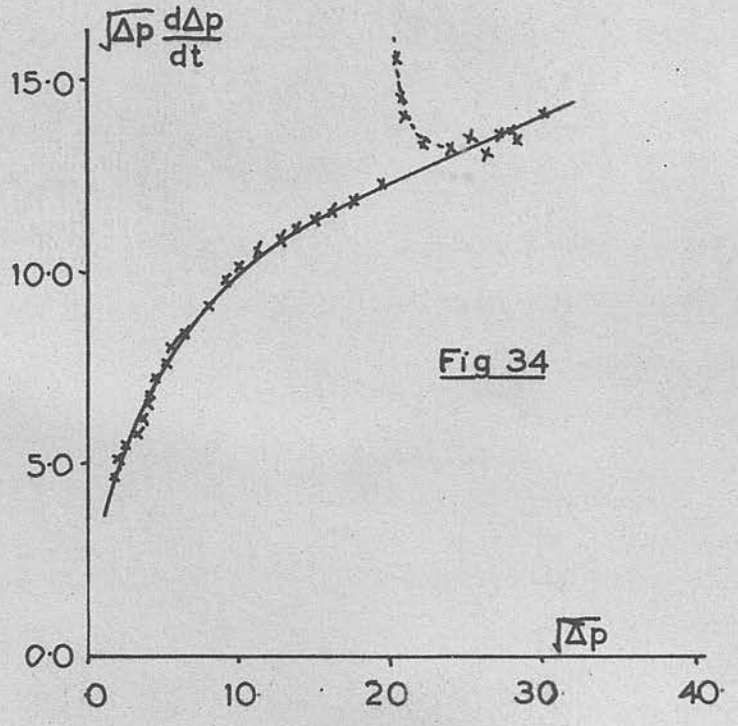

√Δp dΔp/dt
15·0
10·0
5·0
0·0
0
10
20
30
40
√Δp

Fig 34

Table XXXII

$\sqrt{\Delta p}$	$d\Delta p/dt$	$\sqrt{\Delta p}.\ d\Delta p/dt$	$\sqrt{\Delta p}$	$d\Delta p/dt$	$\sqrt{\Delta p}.\ d\Delta p/dt$
1.58	2.88	4.55	6.20	0.73	4.53
1.87	2.64	4.93	6.59	0.67	4.42
2.35	2.18	5.12	6.96	0.64	4.45
2.74	1.85	5.06	7.30	0.60	4.38
2.92	1.73	5.05	7.65	0.59	4.51
3.24	1.52	4.92	7.90	0.57	4.49
3.53	1.35	4.76	9.35	0.44	4.11
3.68	1.32	4.85	10.60	0.37	3.96
3.94	1.23	4.85	11.72	0.34	4.01
4.18	1.14	4.65	12.73	0.30	3.86
4.30	1.11	4.77	13.70	0.28	3.81
4.52	1.05	4.74	14.58	0.26	3.76
4.74	1.02	4.83	15.41	0.24	3.70
4.85	1.00	4.85	16.19	0.22	3.49
5.05	0.93	4.69	21.10	0.145	3.06
5.24	0.89	4.66	24.60	0.110	2.59
5.33	0.86	4.58	27.12	0.088	2.38
5.79	0.81	4.69	27.44	0.083	2.28

Instead of, as in the case of O_2 and NO uptakes, plotting $\Delta p \frac{d\Delta p}{dt}$ against Δp it was necessary to have $\sqrt{\Delta p}.\frac{d\Delta p}{dt}$ against $\sqrt{\Delta p}$ in order to obtain a linear relationship.

$$\text{i.e.} \quad \frac{d\Delta p}{dt} = K\left(\frac{\Delta p_\infty - \Delta p}{\Delta p}\right) \qquad --(1)$$

for O_2 and NO uptakes on water bound films but:-

$$\frac{d\Delta p}{dt} = K\left(\frac{\sqrt{\Delta p}_\infty - \sqrt{\Delta p}}{\sqrt{\Delta p}}\right) \qquad --(2)$$

for oxygen uptake on ammonia treated films. Whereas equation (1) would indicate removal of oxygen and nitric oxide molecules from the gas phase

equation /

equation (2) suggests that the oxygen was removed from the gas phase in the form of atoms. In other words, there may have been a direct dissociative adsorption of oxygen on the surface of an ammonia treated film.

$$O_2 \text{ gas} \rightleftharpoons 2(O) \text{ surface.}$$

The extrapolated value of $\Delta_\infty p$ was $(48.7)^2$ divs. and equivalent to 970 μ/g.

Products of Illumination.

An analysis of the gas phase showed the presence of only 3.0 divs. of condensible gas. This amount was negligible compared with the observed pressure decrease of Δp = 753.3 divs. and it can be taken that the decrease of pressure Δp was due to removal of oxygen. Nitric oxide and nitrogen were absent from the gas phase products.

The products obtained in degassing the illuminated film at 25°C and 10^{-5} mm. were examined at intervals. Water and small amounts of nitrous oxide and ammonia were evolved:-

Table XXXIII

Products	0-2 hours.	2-14 hours.	14-40 hours	Total.
H_2O	18.3 μ	2.2 μ	4.3 μ	24.8 μ
N_2O	3.2	0.4	0.15	3.75
NH_3	3.2	1.9	1.0	6.1

Oxygen uptake Δp = 753.3 divs. = ΔO_2 = 31.6 μ

Nitrite extimation ΔNO_2^- = 0.8 μ (approx.)

The ratio $\Delta O_2 : \Delta H_2O : \Delta N_2O : \Delta NO_2^-$ = 31.6:24.8:3.75:0.8

The yield of N_2O was low and only a trace of nitrite was detectable on extraction with water.

The /

The extrapolated pressure decrease ($\Delta_{\infty} p$) was equivalent to 970 μ moles O_2/gm. i.e., 6 x 162 μ/gm. showing that 6 oxygen molecules reacted with each supposed site. It has already been established that 162 μ moles unit sites /gm. each take up 4 ammonia molecules and the possible photo-reaction was then between $6O_2$ and 4 NH_3 per site, on the assunption that the O_2 and NH_3 adsorption sites were the same and that no independent oxygen adsorption occurs. While the stoichiometric relationship between O_2 and water supports an equation of the type:-

$$6\,O_2 + (4\,NH_3)_{ads.} \xrightarrow{light} 4\,H_2O + (H_4N_4O_8)_{ads.}$$

the small amounts of N_2O and NO_2^- can only be explained by a partial decomposition of $(H_4N_4O_8)_{ads.}$ This will be further enlarged upon in the general discussion of the results.

PHOTO-OXIDATION OF AMMONIA AT A HIGH PARTIAL PRESSURE.

A preliminary experiment on film 13 showed that the illumination of an oxygen ammonia mixture gave rise to a very large pressure decrease (Fig.34) with $\sqrt{\Delta p}.\frac{d\,\Delta p}{dt}$ an increasing quantity(cf.Figs.33).

Film 13

Wt. Sample II	0.0561 gms.
Reaction Volume	33.9 mls.
Ammonia pretreatment	zero
Initial ammonia pressure	19.0 mm. (96.1 μ)
Initial oxygen pressure	50.6 mm.
Gauge sensitivity	0.0230 mm./div.

After noting the pressure decrease on illumination in relation to time a plot from derived values $\sqrt{\Delta p}.\frac{d\,\Delta p}{dt}$ against $\sqrt{\Delta p}$ (see Fig.34) showed /

showed that the pressure decrease $\Delta_{\infty}p$ was not obtainable by this method. If the presence of ammonia in excess of that chemisorbed by replacement of water had no effect and that a process occurred on film 13 identical to film 11 the extrapolated value of $\Delta_{\infty}p$ would have been 34.8^2 divs. From Fig. 34 it is quite obvious that this value would have been exceeded. Data given in Table XXXIV.

Table XXXIV.

Δp	$\frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$
2	3.18	30	1.46	104	0.99	256	0.72	512	0.56
3	2.92	32.5	1.43	109	0.98	263	0.72	526	0.58
4	2.77	35	1.40	115	0.95	270	0.72	540	0.58
5	2.41	37.5	1.35	125	0.91	277	0.72	553	0.58
6	2.21	40	1.32	135	0.90	285	0.72	568	0.56
7	2.14	45	1.26	155	0.87	292	0.70	582	0.56
8	2.07	50	1.21	165	0.84	307	0.68	597	0.56
9	2.00	55	1.20	171	0.83	323	0.67	643	0.52 ⊠
10	1.94	60	1.18	175	0.82	340	0.66	728	0.52
12	1.83	65	1.15	185	0.82	352	0.65	754	0.51
14	1.69	70	1.14	196	0.78	372	0.64⊠	780	0.49
16	1.68	75	1.11	211	0.78	415	0.74	804	0.48
18	1.65	80	1.08	219	0.76	433	0.70	828	0.49
20	1.61	85	1.07	227	0.75	450	0.66	852	0.49
22.5	1.57	90	1.05	234	0.74	466	0.64	876	0.48
25	1.53	95	1.03	242	0.73	479	0.60		
27.5	1.50	100	1.01	249	0.73	492	0.60		

⊠ Illumination interupted for 16 hours.

The reaction vessel was fitted with a side arm which allowed ammonia and other condensible products to be removed from the gas phase. By this method, with due allowance made for the effect on the pressure due to refrigeration of the side arm, it was possible to measure the initial and final concentrations of ammonia and oxygen in the gas phase, and thereby calculate the uptake of oxygen.

Initial /

Initial total pressure		69.6 mm.
Final Total pressure		48.2 mm.
∴ Pressure decrease on illumination		21.4 mm.
Initial oxygen pressure		69.4 mm. (corrected)
Final oxygen pressure		33.0 mm. (corrected)
Oxygen uptake	=	16.6 mm.
	=	29.9 μ
∴ Decrease in Ammonia pressure		5.0 mm.

A full analysis of the products obtained on evacuation and aqueous extraction was:-

Residual Ammonia	45.7 μ
Water	61.1 μ
Nitrite	3.3 μ
Nitrous oxide	none detected

Total reactants:-

ΔO_2	=	29.9 μ
ΔNH_3	=	50.4 μ

Total products identified:-

ΔH_2O	=	68.1 μ
ΔNO_2^-	=	3.3 μ

A large amount of water would have been obtained by displacement with an equal amount of ammonia. (Maximum H_2O displacement = 650 x 0.0561 μ = 36.5 μ).

This preliminary experiment established that a very large uptake of oxygen resulted in the illumination of an ammonia-oxygen mixture in contact with titanium dioxide. It was not possible to determine the extrapolated gas uptake /

uptake by the methods adopted but it is quite probable that the relative extent was several times greater than that of film 11. The only major product identified was water. It is to be assumed that there was a nitrogenous product adsorbed on the surface of the illuminated film, the nature of which was unobtainable from the above data but by analysis was shown not to be NH_2OH, N_2H_4 or HNO_3.

Attempted identification tests (42).

NH_2OH Ammoniacal Cupric ferricyanide did not give a white ppt. of Cuprous ferricyanide. Ind. limit = 0.2×10^{-6} gm.

N_2H_4 Aqueous extrat + saturated aqueous solution of salicylaldehyde, no cloudiness of salicylaldazine. Idn. limit 0.1×10^{-6} gms.

PHOTO-OXIDATION OF AMMONIA ON TITANIUM DIOXIDE.

Beyond establishing the extremely large oxygen uptake, with the subsequent formation of water as a major product, film 13 yielded little further information. An improved experiment upon film 14 was carried out under the following conditions:-

(a) Complete water displacement was carried out by saturating the film with ammonia until no water was recovered in the desorbed ammonia. The film was then evacuated at 10^{-5} mm. Hg. overnight before admitting oxygen and more ammonia. Water produced on illumination would then be due to oxidised ammonia.

(b) A small sample weight, a large reaction volume and a relatively large amount of ammonia were employed in order to keep the relative change in ammonia concentration and pressure as small as possible during the entire illumination.

Film 14.

Film 14.

Wt. Sample II	0.0288 gms. (wt. after evacuation)
Reaction Volume	59.6 mls.
Ammonia pretreatment	18.7 μ (due to water displacement)
Initial ammonia pressure	25.0 mm.
Initial oxygen pressure	77.6 mm.
Gauge sensitivity	0.0230 mm./div.

Addition of 109.3 μ NH_3 to the pretreated film gave an equilibrium ammonia pressure of 25.0 mm. Had no sorption occurred on this addition the theoretical ammonia pressure would have been 34.0mm. This implies that after the chemisorption of 18.7 μ NH_3 a further physical sorption of 29.0 μ NH_3 had occurred.

Illumination of film 14 produced a pressure decrease which was noted in relation to time. (see Table XXXV).

Table XXXV /

Table XXXV

t(mins)	Δp(divs)	t	Δp	t	Δp	t	Δp
0	0.0	26	10.0	343	61.3	1358	160.8
0.5	0.6	28	10.4	351	62.2	1381	164.4
1	0.9	30	11.2	358	63.3	1413	166.8
1.5	1.2	35	12.4	371	64.4	1442	169.6
2	1.7	39	13.4	382	66.1	1473	172.6
3	2.2	44	14.8	393	67.1	1493	174.5
4	2.5	48	15.7	404	68.1	1532	177.5
5	3.0	53	16.5	413	69.3	1574	181.6
6	3.3	61	18.2	431	71.2	1591	183.0
7	3.9	67	19.7	444	73.1	1625	186.7
8	4.2	76	21.3	458	74.4	1753	201.0
9	4.5	85	23.1	473	76.1	1789	204.0
10	5.1	98	25.3	488	77.7	1732	207.8
11	5.3	107	27.0	504	79.3	1867	211.8
12	5.8	123	30.0	529	82.2	1897	213.9
13	6.1	132	31.4	546	83.9	1915	215.4
14	6.3	141	32.8	1138	140.8	1971	221.7
15	6.5	146	33.3	1154	142.4	2258	280.3
16	7.1	165	34.8	1173	143.7	2617	283.7
17	7.3	170	35.3	1180	144.4	2664	287.2
18	7.7	183	37.4	1208	146.9	2723	293.5
19	8.0	192	39.0	1239	150.4	2749	295.8
20	8.1	202	40.4	1255	151.7	2806	301.7
21	8.4	215	42.9	1273	153.4	2837	304.7
22	9.0	227	44.2	1296	154.5	2877	309.8
23	9.3	335	60.2	1319	157.4	2890	310.0
24	9.3					2942	315.2
						2971	318.1

A plot of $\sqrt{\Delta p}$ against $\sqrt{\Delta p}\frac{d\Delta p}{dt}$, as for film 11, did not show linearity and it was necessary to resort to a relationship observed to hold for the oxygen uptake on acetone bound fils:-

$$\text{i.e. antilog } \frac{d\Delta p}{dt} = K\left(\frac{1}{\Delta p} - \frac{1}{\Delta_{\infty} p}\right) \qquad -(1)$$

In the case of film 14 $\frac{1}{\Delta_{\infty} p}$ was very small compared to $\frac{1}{\Delta p}$ and the expression 1 can be put in the form:-

$$\frac{d\Delta p}{dt} = -\log \Delta p + \log K \qquad -(2)$$

by /

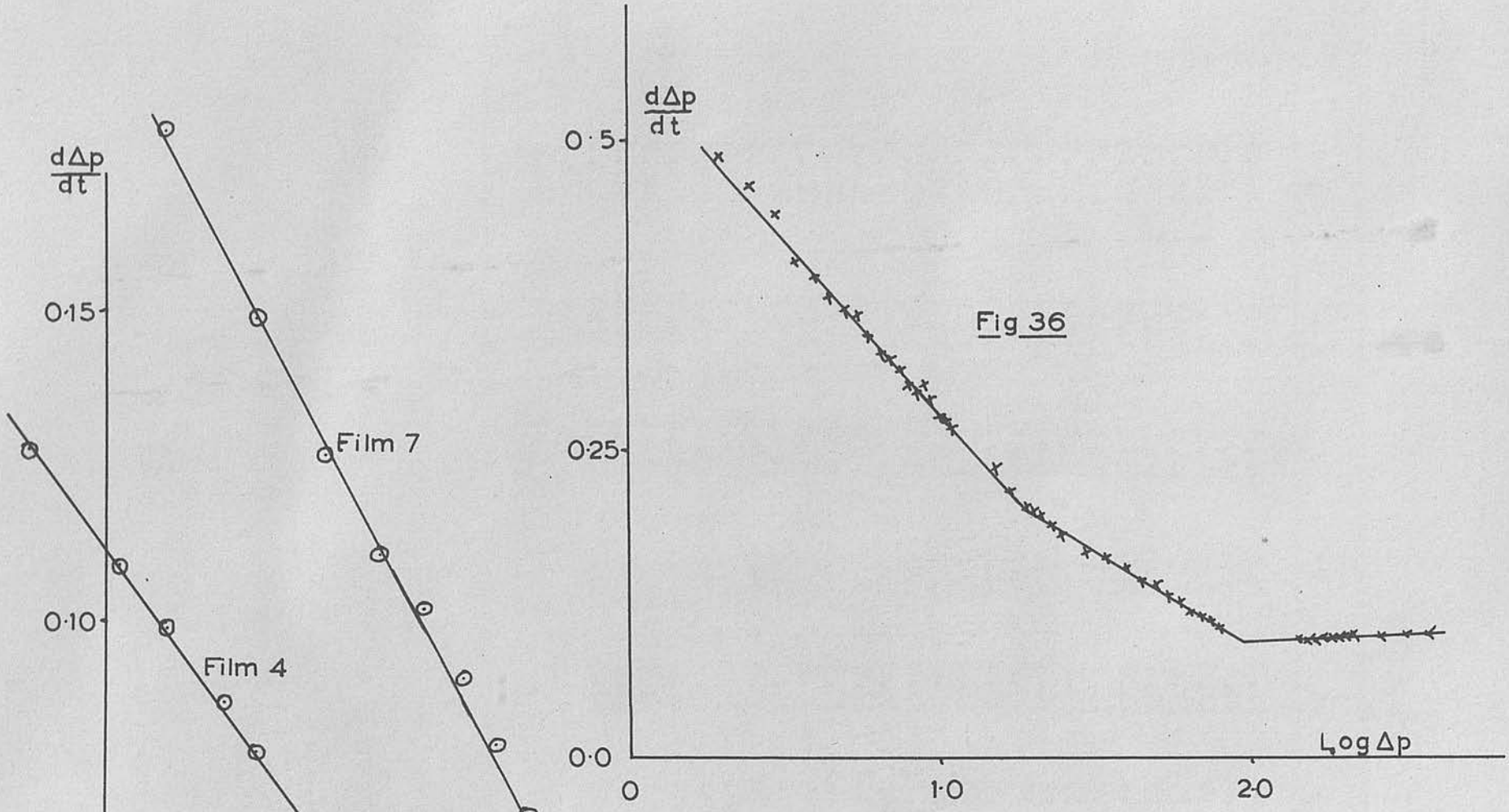

dΔp/dt
0·5
0·25
0·0
0
1·0
2·0
Log Δp

Fig 36

dΔp/dt
0·15
0·10
0·05
0·00
Film 7
Film 4
1·0
1·5
2·0
Log Δp

Fig 35

by taking the log of both sides. The derived values of $\frac{d\Delta p}{dt}$ and log Δp are given in Table XXXVI. It is noted in passing that a plot of $\frac{d\Delta p}{dt}$ against log Δp gave linear plots for films 1 - 9 in the initial stages of the gas uptakes and in the case of acetone bound films the extrapolated values of log Δp gave very close agreement with each other (see Fig. 35).

Fig. 36 shows graphically the derived values in Table XXXVI. It is seen that a constant rate process started at log Δp = 1.99, i.e. $\Delta p \doteq 250$ μ/gm. after a break in linearity at $\Delta p \doteq 50$ μ/gm. Interpretation of the breaks, at this stage, is not possible but it is probable that they were due to some change in the oxidation mechanism.

Table XXXVI

Δp	$\frac{d\Delta p}{dt}$	log Δp	Δp	$\frac{d\Delta p}{dt}$	log Δp
0.5	0.98	1.699	21	0.196	1.322
1.0	0.77	0.000	23	0.187	1.362
1.5	0.59	0.176	25	0.181	1.398
2.0	0.485	0.301	30	0.167	1.477
2.5	0.463	0.398	35	0.163	1.544
3.0	0.439	0.477	40	0.154	1.602
3.5	0.403	0.544	45	0.144	1.653
4.0	0.388	0.602	50	0.138	1.699
4.5	0.374	0.653	55	0.132	1.740
5.0	0.364	0.699	60	0.125	1.778
5.5	0.358	0.740	65	0.117	1.813
6.0	0.343	0.778	70	0.114	1.845
6.5	0.327	0.813	75	0.110	1.875
7.0	0.323	0.845	60	0.106	1.903
7.5	0.314	0.875	145	0.096	2.161
8.0	0.300	0.903	155	0.094	2.190
8.5	0.298	0.929	165	0.095	2.218
9.0	0.300	0.954	175	0.096	2.243
9.5	0.291	0.978	185	0.096	2.220
10.0	0.276	1.000	195	0.097	2.290
10.5	0.272	1.021	205	0.098	2.312
11	0.267	1.041	215	0.099	2.332
15	0.234	1.176	270	0.099	2.43
17	0.216	1.230	315	0.098	2.50
19	0.202	1.279	375	0.098	2.58
20	0.199	1.301			

Products /

Products from film 14.

Total observed pressure decrease (378 divs). $\Delta p = 23.4\ \mu$

(a) Analysis of Gas phase:-

$\Delta_g NH_3 = 76.2\ \mu$

$\Delta_g H_2O = 3.84\ \mu$

$\Delta_g N_2O = 0.0\ \mu$

(b) Prolonged evacuation(48 hrs.):-

$\Delta_l NH_3 = 6.4\ \mu$

$\Delta_l H_2O = 18.2\ \mu$

$\Delta_l N_2O = 1.5\ \mu$

(c) Residual film:-

$\Delta NO_2^- = 1.4\ \mu$

Ammonia oxidised	$26.7\ \mu$ [= 109.3 - (76.2 + 6.4)]
Water produced	$22.0\ \mu$ [= 3.8 + 18.2]
Pressure decrease, Δp.	$23.4\ \mu$
Nitrous oxide produced	$1.5\ \mu$
Nitrite (NO_2^-) produced	$1.4\ \mu$

Summary of film 14

(1) A constant rate process has been observed in the final stages of the photo-uptake of gas from an oxygen-ammonia mixture. It is probable that these features represent an oxidation of surface sorbed ammonia.

(2) The major detectable product was water. Nitrous oxide was produced in very small amounts and together with nitrite constituted only a very small proportion of the non-recoverable ammonia. No NH_2OH, N_2H_4 or HNO_3 were detected.

(3) /

(3) From the analysis of the products it was not possible to determine if the 18.7 μ chemisorbed ammonia took a part in the constant rate process.

PHOTO-CATALYTIC OXIDATION OF AMMONIA AND THE PART PLAYED BY PRE-SORBED AMMONIA.

The above summary might be taken to suggest that the ammonia sorbed at the expense of water on the surface of the titanium dioxide may have provided a base from which ammonia sorbed from the gas phase could be oxidised. By the examination of the products of a series of ammonia oxidations on film 15, it was seen how the constant rate oxidation stemmed from a surface complex built upon the presorbed ammonia.

Film 15.

Wt. Sample II	0.0545 gms (wt. after evacuation)
Reaction Volume	33.9 mls.
Ammonia pretreatment	35.4 μ sorbed (35.4 μ H_2O desorbed)
Gauge sensitivity	0.0230 mm./div.

The reaction vessel was fitted with a side arm into which measured quantities of ammonia were condensed. The ammonia pressure in the reaction vessel was determined by allowing the ammonia to evaporate and reach equilibrium (a). Oxygen was admitted to the reaction vessel with the ammonia condensed in the side arm. The combined oxygen-ammonia pressure in the reaction vessel was measured after the two gases had interdiffused and reached a steady equilibrium (b) (after 1 hr.). The initial oxygen pressure was taken to be the difference between the observed values of (a) and (b). The pressure decrease (Δp) occurring within the reaction vessel on illumination was noted in relation to time (t mins.). A plot of $\frac{d\Delta p}{dt}$ against $\log \Delta p$ is shown /

shown in fig. 37 to illustrate the magnitude of the photo process. The rate of pressure decrease observed during the first illumination was relatively larger than that observed during the second, third and fourth illuminations. Up to about Δp = 500 divs. an approximately constant rate process was observed with the latter three illuminations.

When the pressure within the reaction vessel had decreased about 2000 divs. (total pressure = c) the gas phase was withdrawn through a cold trap until the pressure had been reduced to $\sim$0.01 mm. All condensible products were then distilled back into the side arm (film in position) and the equilibrium pressure they gave at 25°C was noted (d). The final oxygen pressure was then taken as being equal to (c - d.) The total oxygen uptake was then equal to (b - a) - (c - d). Thorough evacuation of the reaction vessel for 24 hrs. was considered sufficient to remove condensible products of analysis. When isolated from the high vacuum system the film was observed to desorb " in the dark" a non-condensible gas which gave a red discharge under an applied voltage. Such a discharge was characteristic of nitrogen. The amount of nitrogen (and also possibly hydrogen) desorbed after evacuation of condensible products, increased after illuminations 1, 2, and 3 and remained approximately the same (after 24 to 48 hrs.) after illuminations 3 and 4. Further measured quantities of ammonia and oxygen were introduced at this stage when the rate of nitrogen desorption was negligibly small.

Table XXXVII gives the absolute pressure of the desorbed gas (Δp divs), in relation to time (t mins.) which occurred after the products from the third illumination had been removed.

Table XXXVII/

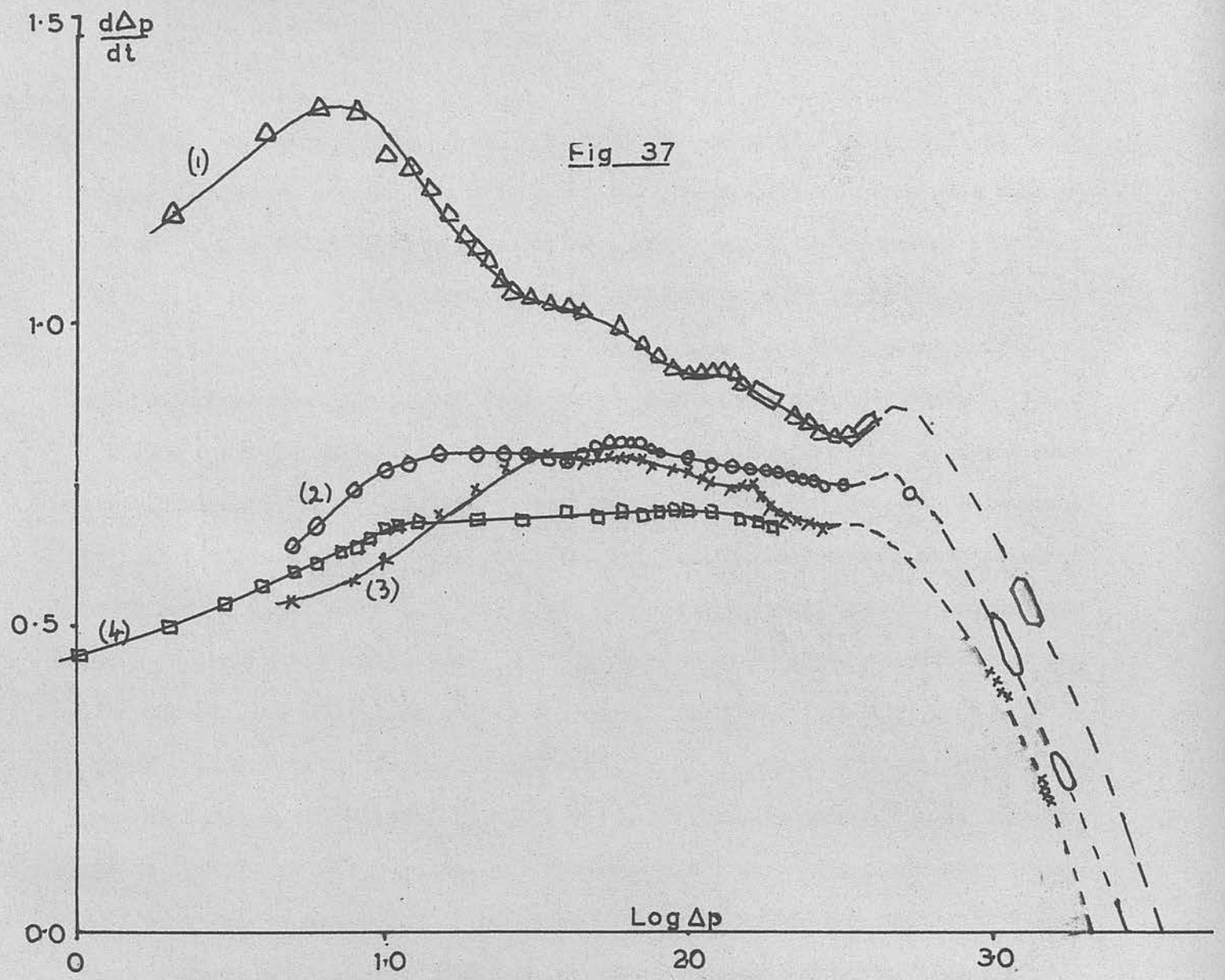

1·5
dΔp/dt
1·0
0·5
0·0
(1)
(2)
(3)
(4)
Log Δp
0
1·0
20
30

Fig 37

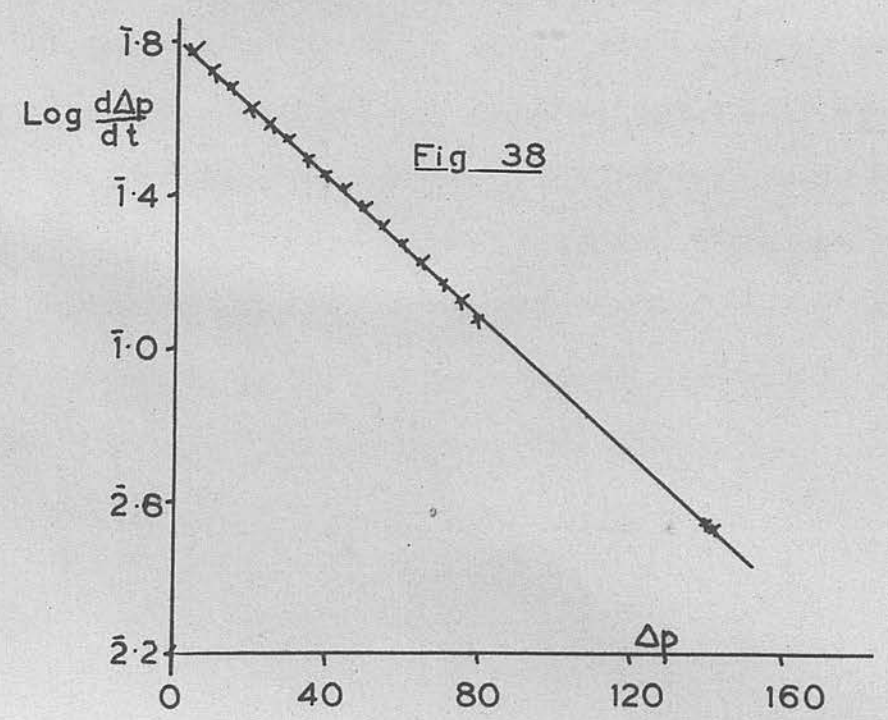

Log dΔp/dt
1̄·8
1̄·4
1̄·0
2̄·6
2̄·2
Δp
0
40
80
120
160

Fig 38

Table XXXVII

t	Δp	t	Δp	t	Δp	t	Δp
0	0.0	53	26.1	237	68.1	1386	140.7
1	0.9	60.5	28.9	287	70.7	1393	148.8
2.5	1.9	82	36.0	324	80.9	1408	141.3
5.5	3.8	94	39.6	351	83.8	1414	141.0
9	6.0	114	44.9	1284	136.7	1435	142.3
16	9.8	122	46.9	1305	137.7	1444	142.7
23	13.3	142	51.6	1316	137.8	1451	142.8
26	14.9	155	54.4	1328	138.2	1458	143.0
31	17.1	168	57.3	1333	138.7	1468	143.2
33	18.0	179	59.6	1341	139.0	1474	143.6
40.5	21.1	188	61.3	1353	139.5	1481	143.8
45	23.0	194	62.6	1365	139.9	1498	144.1
49	24.7	207	63.7	1377	140.3	1504	144.6

Derived values in Table XXXVIII show the desorption to conform to the Roginsky-Zeldovich equation:-

$$\log \frac{d\Delta p}{dt} = b(\Delta p' - \Delta p) \qquad \text{(Fig. 38)}$$

where b has a + ve value = .00914.

The process was one of "dechemisorption".

Table XXXVIII

Δp	$\frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$	Δp	$\frac{d\Delta p}{dt}$	$\log \frac{d\Delta p}{dt}$
5	0.602	$\bar{1}.780$	50	0.236	$\bar{1}.373$
10	0.526	$\bar{1}.721$	55	0.208	$\bar{1}.318$
15	0.476	$\bar{1}.678$	60	0.187	$\bar{1}.272$
20	0.424	$\bar{1}.627$	65	0.168	$\bar{1}.225$
25	0.382	$\bar{1}.582$	70	0.149	$\bar{1}.173$
30	0.354	$\bar{1}.549$	75	0.132	$\bar{1}.124$
35	0.312	$\bar{1}.494$	80	0.118	$\bar{1}.079$
40	0.282	$\bar{1}.450$	140	0.0358	$\bar{2}.554$
45	0.260	$\bar{1}.415$	142	0.0342	$\bar{2}.534$

The /

Fig 39

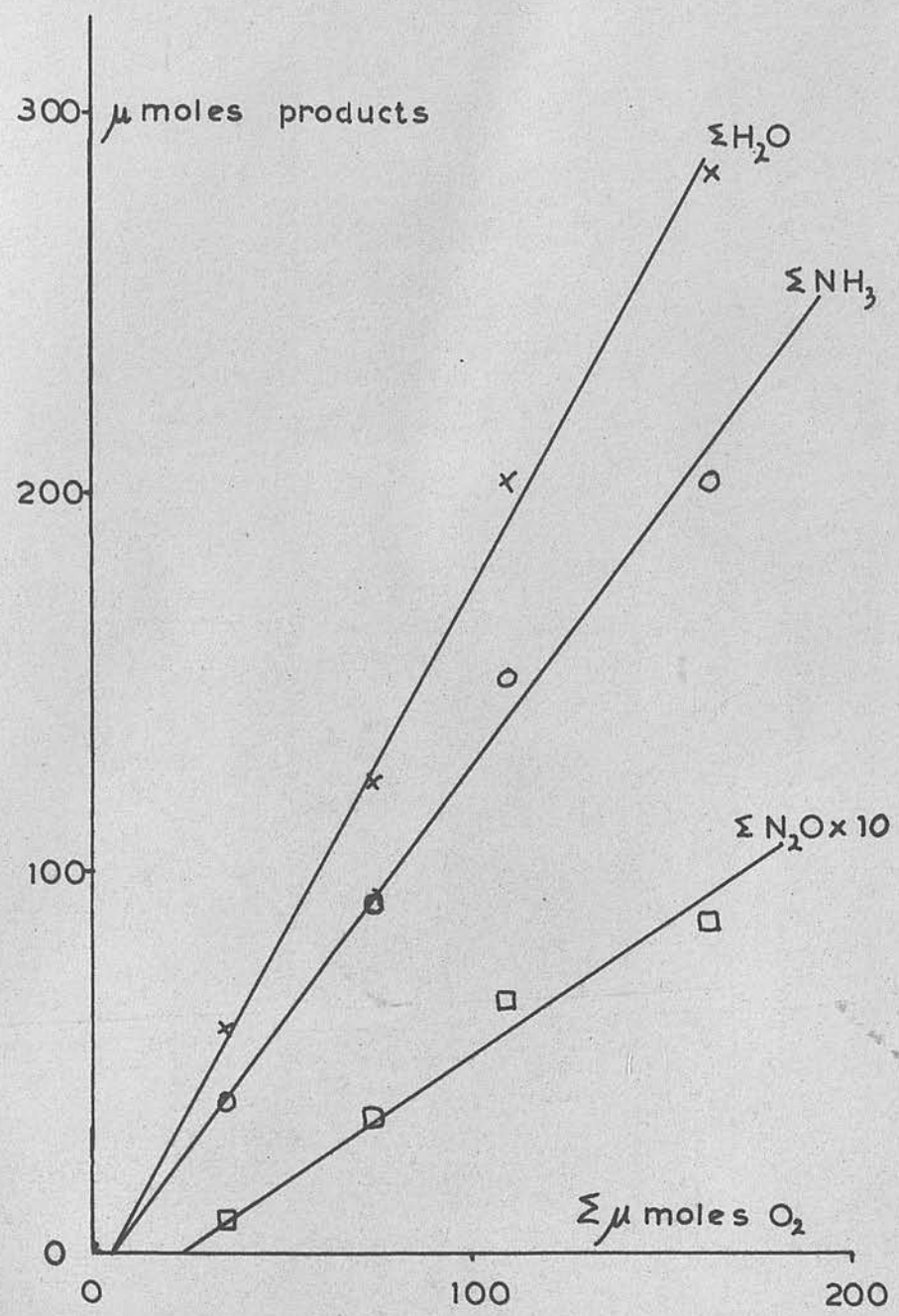
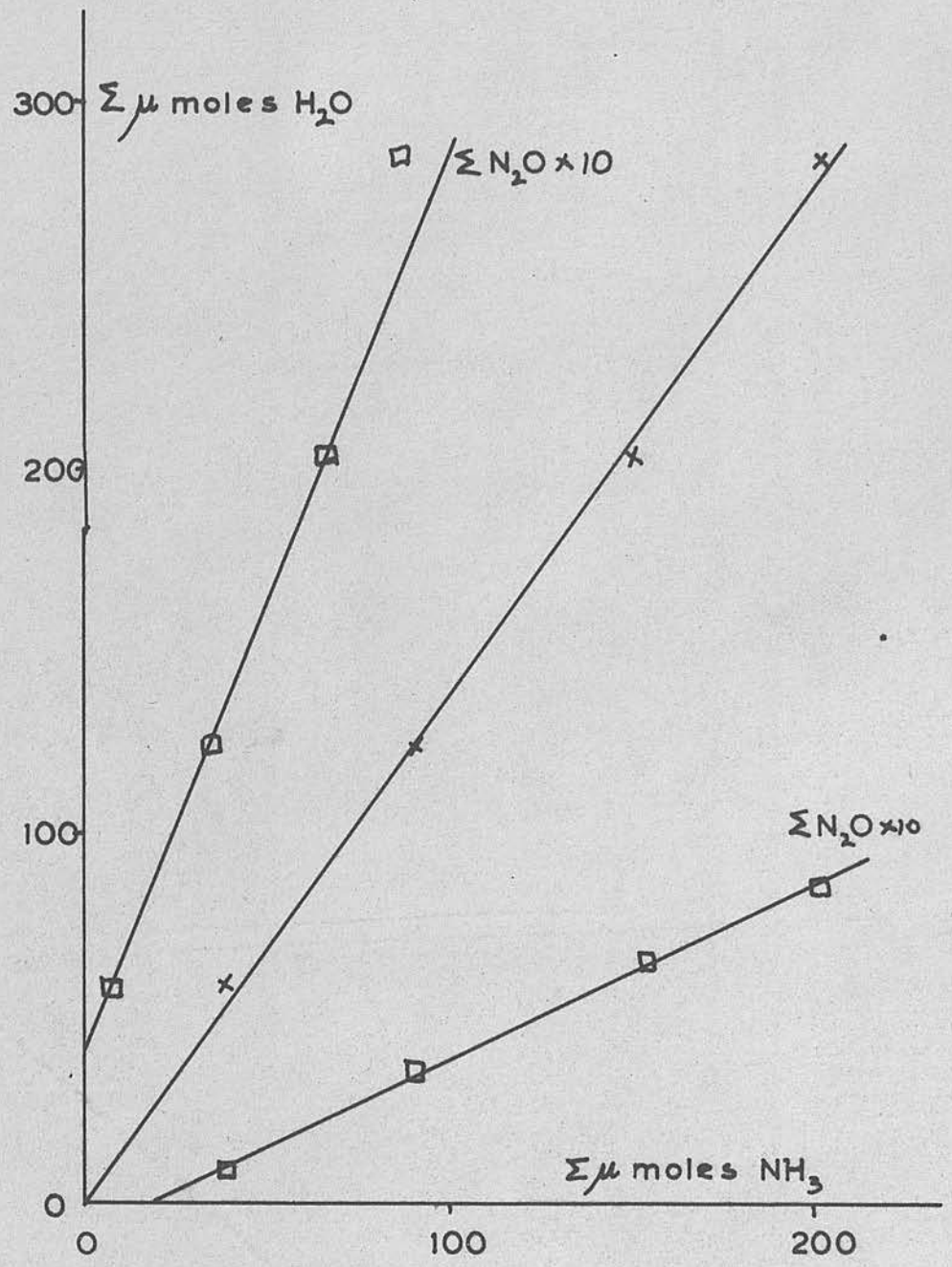

300
μ moles products
ΣH2O
ΣNH3
200
ΣN2O×10
100
ΣμmolesO2
0
0
100
200

Fig 40


300
Σμ moles H2O
ΣN2O×10
200
100
ΣN2O×10
Σμ moles NH3
0
0
100
200

The results for four consecutive illuminations of film 15 are given in Table XL.

Table XXXIX

REMARKS	UNITS	1	2	3	4
Initial Ammonia Present	μ	108.1	107.0	102.7	103.2
Initial Ammonia Pressure	mm.	35.2	31.9	28.3	26.8
Final $NH_3 + H_2O + N_2O$ Pressure	mm.	22.1	13.3	11.7	11.8
Initial O_2 Pressure	mm.	61.5	102.3	107.3	113.0
Final O_2 Pressure	mm.	48.1	81.2	88.7	83.8
Oxygen Consumed	μ	35.9	38.5	35.0	53.3
Ammonia in Products	μ	69.1	55.4	43.0	51.1
Ammonia Oxidised	μ	39.0	51.6	59.7	52.1
Water Produced	μ	58.0	65.9	79.2	81.6
N_2O Produced	μ	0.8	2.7	3.1	2.0

From the residual film 3.3 μ NO_2^- was obtained on extraction with water.

Estimated nitrogen desorbed.

Table XL.

After Illumination	ΔN_2 Desorbed (μ)	$\Sigma\Delta N_2$ (μ)
1	0.2	0.2
2	1.5	1.7
3	7	9
4	7	16

Accumulative quantities of reactants and products are given in Table XLI.

Table XLI

Illuminations	$\Sigma\Delta O_2$	$\Sigma\Delta NH_3$	$\Sigma\Delta H_2O$	$\Sigma\Delta N_2O$
1	35.9 μ	39.0 μ	58.0 μ	0.8 μ
1 + 2	74.3	90.6	123.9	3.5
1 + 2 + 3	109.3	150.3	203.1	6.6
1 + 2 + 3 + 4	162.6	202.4	284.7	8.6

and are shown graphically in Figs. 39 and 40. As drawn, any two reactants/

reactants or products can be graphed against each other and a linear relationship observed. The accuracy of the analysis was such that it must be taken as unlikely that all plots can be accommodated on lines drawn through the origin. Nitrous oxide which was produced in a very low yield with respect to water, would appear to be a by-product. Extrapolation of its linear relationships to oxygen, ammonia and water showed that 24 μ O_2 and 20 μ NH_3 had reacted and 40 μ H_2O was produced before any N_2O was produced. On the assumption that these extrapolations are valid it is also seen that ammonia reacted after the uptake of 5 μ O_2. Water was produced at the same time as ammonia reacted, i.e. after the uptake of 5 μ O_2. The ratio of the intercepts are:-

	O_2-H_2O	:	O_2-NH_3	:	O_2-N_2O	:	NH_3-N_2O	:	H_2O-N_2O	
=	5	:	5	:	24	:	20	:	40	(μ)
=	92	:	92	:	440	:	367	:	734	(μ/gm.)
=	$\frac{1}{2}$ x 184	:	$\frac{1}{2}$ x 184	:	$2\frac{1}{2}$ x 176	:	2 x 183	:	4 x 186	

and can be taken as showing the building up of a surface complex which was capable of promoting a light induced catalytic oxidation of ammonia.

Such a complex could be built on a surface site in the following manner:-

$$(\text{site}).2\,H + (O) \xrightarrow{\text{light}} (\text{site}) + H_2O, \qquad (1)$$

The site must have at least two oxidisable hydrogen atoms. This would be followed by the addition of two ammonia molecules:-

$$(\text{site}) + 2\,NH_3 \longrightarrow (\text{site}).2\,NH_3, \qquad (2)$$

which could be oxidised by a further four oxygen atoms:-

$$(\text{site}).2\,NH_3 + 4(O) \xrightarrow{\text{light}} (\text{site})N_2O + 3\,H_2O. \qquad (3)$$

At this stage the total process has been:-

$$(\text{site}).2\,H + 5(O) + 2NH_3 \xrightarrow{\text{light}} (\text{site}).N_2O + 4\,H_2O \quad (1 + 2 + 3)$$

From this simple scheme it is quite obvious how N_2O may have been produced.

However,/

However, experiment showed that N_2O was produced in a low yield and that the nitrogen in the total products constituted only a small fraction of the total ammonia oxidised.

Balance of elements.

Oxygen	Total reacted oxygen	$= \Sigma\Delta O_2 =$	157 μ moles. O_2 =	314 μ (O)[⊠]
	Oxygen in products H_2O		284.7 μ (O)	
		N_2O	8.6 μ	
		NO_2^-	6.6 μ	
			Total =	300 μ (O)
			Balance =	14 μ (O)
Nitrogen	Total reacted nitrogen(NH_3) $= \Sigma\Delta NH_3$			= 202.4 μ (N)
	Nitrogen in products	N_2O	17.2 μ	
		NO_2^-	3.3 μ	
		N_2	32.0 μ	
			Total =	52.5 μ (N)
			Balance =	150 μ (N)

⊠ The experimentally determined amount of reacted oxygen(162.6μ) was, from Figs. 39 and 40, slightly high. On the basis of the ammonia and water analysis the figures 157 μ moles was taken to be the more accurate estimate of $\Sigma\Delta O_2$.

Hydrogen	Total reacted hydrogen(NH_3) = 3 x 202.4 $= (3 \times \Sigma\Delta NH_3)$		= 607.2 μ (H)
	+ 2(H) from each site = 2 x 170[⊠] x 0.0545 (eq.1)		18.5 μ
		Total =	625.7 μ
	Total hydrogen in products (H_2O)		569.4 μ (H)
		Balance =	56.3 μ (H)

⊠ 170 μ/gm. was taken to be the mean value of the number of sites/gm.

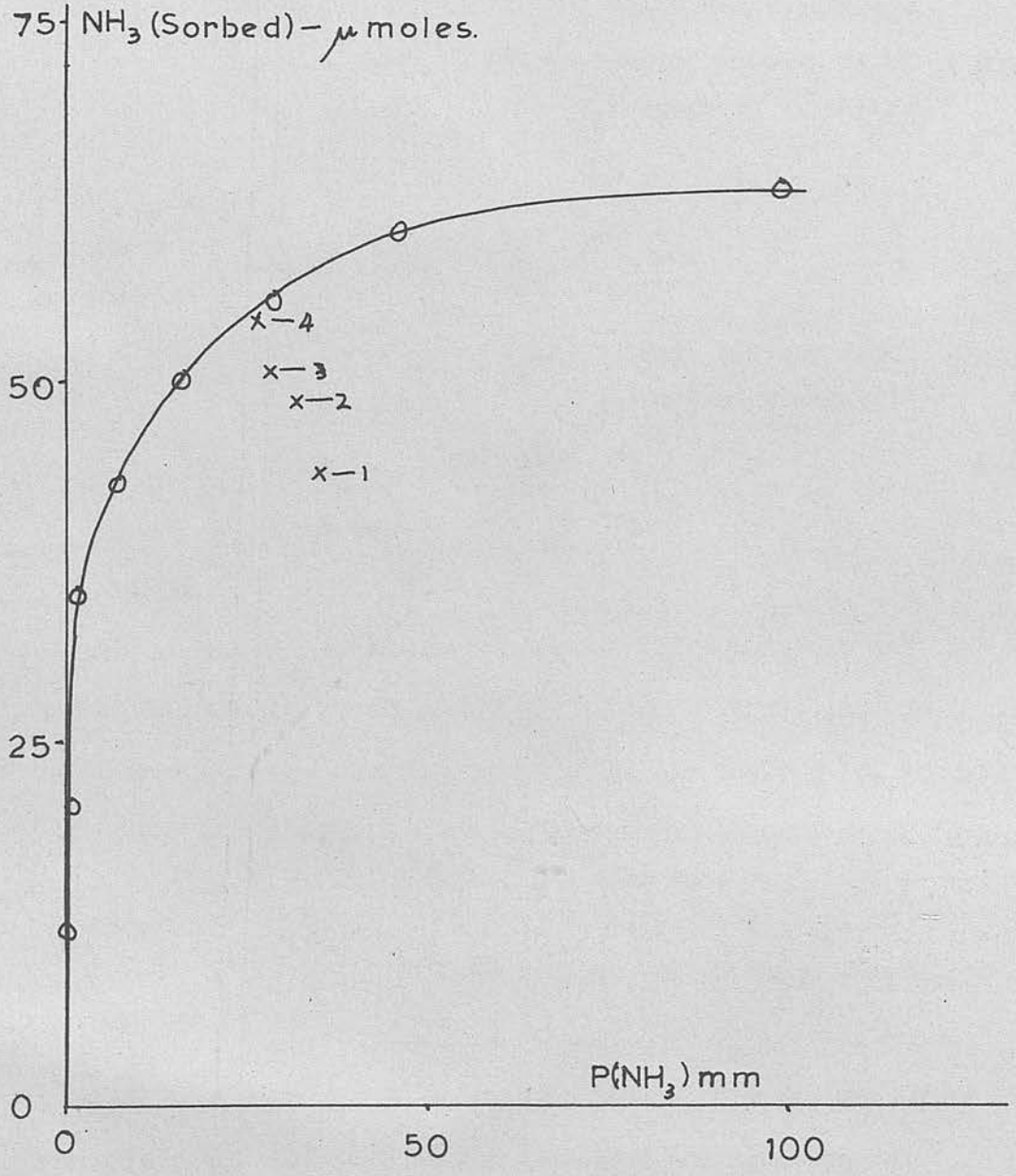
The products not accounted for by H_2O, N_2O, NO_2^- measurements were in the ratio:-

14 (O) : 150 (N) : 56.3 (H)

= 0.3 (O) : 3.0 (N) : 1.1 (H)

If /

Fig 4 2



If the complex contained oxygen (equation 3) the small balance of 14 μ (O) can be accounted for approximately. One oxygen atom/site = 9 μ (O).

The remaining reactants are hydrogen and nitrogen in the ratio (N):(H) = 3.0:1.1. This corresponds to hydrazoic acid HN_3. Extraction of HN_3 by alkali from the residual film, failed to give a positive test for an azide on analysis. (The extraction was made acid,(H_2SO_4), warmed, and HN_3 vapour tested for by colouration of a ferric chloride droplet.(42)).

The physical evidence of nitrogen desorption occurring after the removal of reaction products supported the formation of HN_3. During the photo process the production of HN_3 would have been accompanied by combination with NH_3 to give ammonium azide ($NH_4.N_3$). NH_4N_3 dissociates, as do most ammonium salts, into NH_3 and HN_3. Fig 41* (43) shows ammonium azide to have a very appreciable vapour pressure at 40°C ($\sim$4-5mm.). The hydrazoic acid must have been retained on the surface while ammonia was desorbed. Only when HN_3 is produced will N_2 be desorbed:-

$$2\ HN_3 \longrightarrow 3\ N_2 + H_2 \qquad (5)$$

The decomposition of hydrazoic acid was not studied in detail and equation 5 might not represent the actual process. It was not established if hydrogen was present in the desorbed nitrogen.

The admission of equal quantities of ammonia to the reaction vessel gave successively decreasing equilibrium pressures (see Table XL). This can be explained by an increase in the number of adsorption centres for ammonia. The presence of adsorbed HN_3 would remove an equivalent amount of ammonia from the gas phase.

In Fig.37 oxidations 1, 2 and 3 appeared to decrease rapidly at decreasing values of $\log \Delta p$, this being in agreement with smaller amounts of oxidisable ammonia or alternatively with greater amounts of NH_3 adsorbed on surface located HN_3. Fig. 42 shows the adsorption isotherm of ammonia and titanium dioxide at 25°C as measured after/

* Fig 41 is opposite page 111

after the fourth oxidation of ammonia. The points marked with an X refer to the observed ammonia equilibrium pressures prior to oxidations 1, 2, 3 and 4.

Uptake of Oxygen on Film 15 in absence of Ammonia.

After evacuating all volatile products and after the nitrogen desorption had reached an immeasurably low rate (after oxidation 3), oxygen was admitted to 50 mm. and the film illuminated. No pressure decrease was observed and no appreciable product was obtained. Over a period of twenty hours illumination the pressure had increased by approximately 1 div., which would roughly coincide with the expected "tail off" of the nitrogen desorption.

The surface complex was not destroyed by illumination in oxygen alone. Ammonia must then have reacted first with the complex and oxidation then followed. The scheme then visualised was:-

$$(\text{site}).N_2O + NH_3 \longrightarrow (\text{site}) + HN_3 + H_2O \quad (4)$$

$$(\text{site}) + 2\ NH_3 \longrightarrow (\text{site}).2\ NH_3 \quad (2)$$

$$(\text{site}).2\ NH_3 + 2\ O_2 \longrightarrow (\text{site}).N_2O + 3\ H_2O \quad (3)$$

Catalytic process $3\ NH_3 + 2\ O_2 \longrightarrow HN_3 + N_2O$

Possible side reaction $(\text{site}).N_2O \longrightarrow (\text{site}) + N_2O$

This and the production of N_2O will be enlarged upon in the discussion.

PHOTO-SEMICONDUCTIVITY IN TITANIUM DIOXIDE

This section although not quite complete, with regard to the preceding experimental parts, illustrates an additional means of attacking problems in surface chemistry by recording changes in electrical conductivity.

Previous work by Simpson (44), Nagle, Lyall and Ritchie (45) of this Department had shown that the illumination of specimens of titanium dioxide caused a decrease in resistance. More accurate and detailed results have since been obtained in close collaboration with Allsopp and Kennedy.

All resistance measurements, were made by a Vibron Electrometer on to a bridge of titanium dioxide (Sample I) at room temperature, across a space of approximately 1 mm. between two platinum electrodes. This was easily prepared from a cement of Sample II (~ 0.02 gms.) with distilled water and subsequently dried out by evacuation. During such evacuation an initial rapid rise, followed by a slow increase in the resistance, was attributed to loss of surface conductivity by evaporation of adsorbed water. Because of this effect, it was never possible to obtain a constant resistance value due to evacuation alone and it was necessary to ensure that a steady resistance value prevailed before causing changes in the conductivity. Normally, evacuation as the only pretreatment, was carried out to give a resistance value of the order of $10^{13\pm1}$ Ω, (Prolonged evacuation would raise the resistance value beyond the working range of the apparatus.) Changes in the resistance value were usually large and runs are best represented graphically by employing $\log_{10}$ (resistance) values.

Vacuum Photoconductivity.

Illumination in vacuo produced a large time dependant decrease in resistance (Figs. 43 and 44). Clearly this must have been due to the excitation /

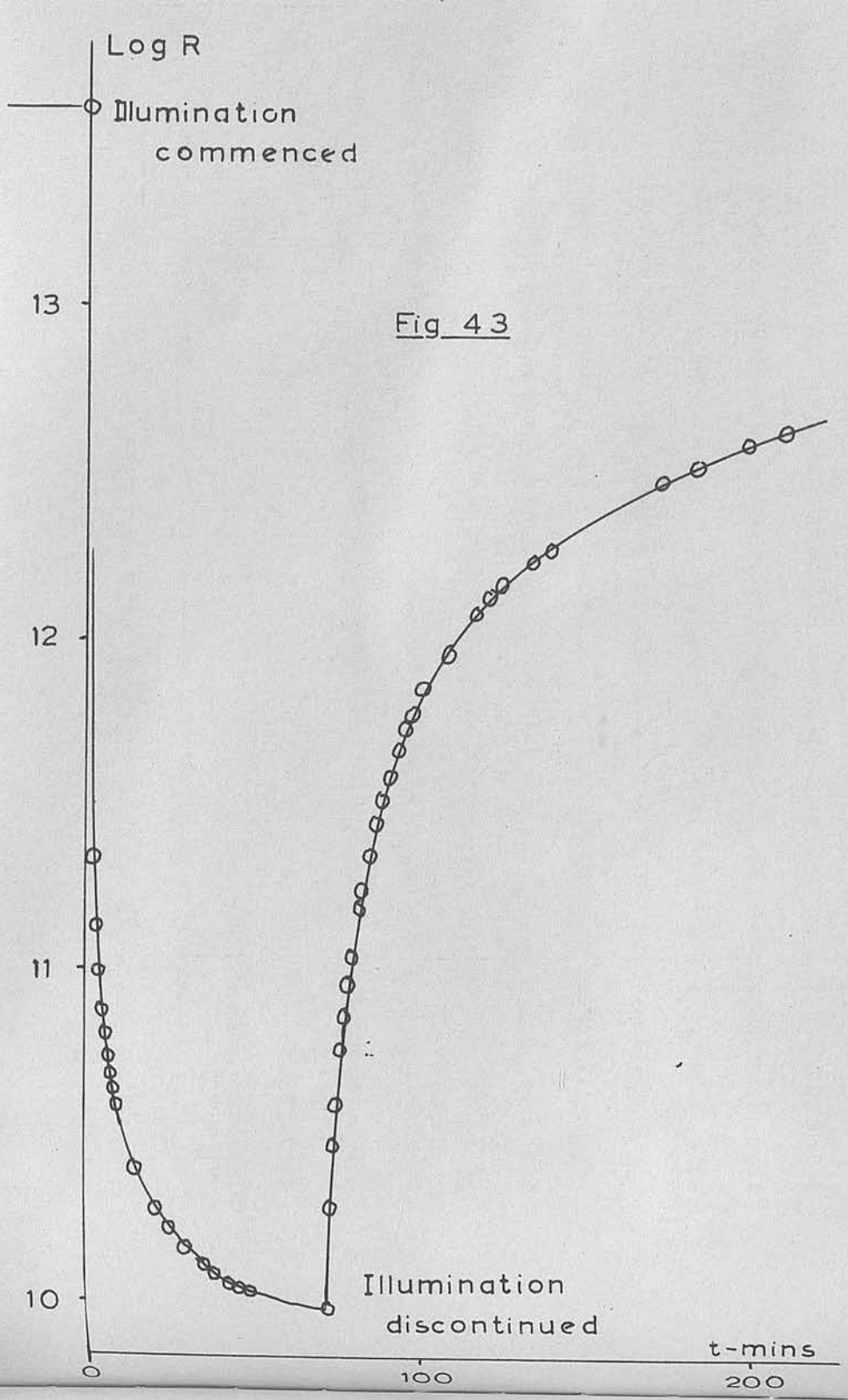

Log R
Illumination commenced
13
12
11
10
Illumination discontinued
t-mins
0
100
200

Fig 43

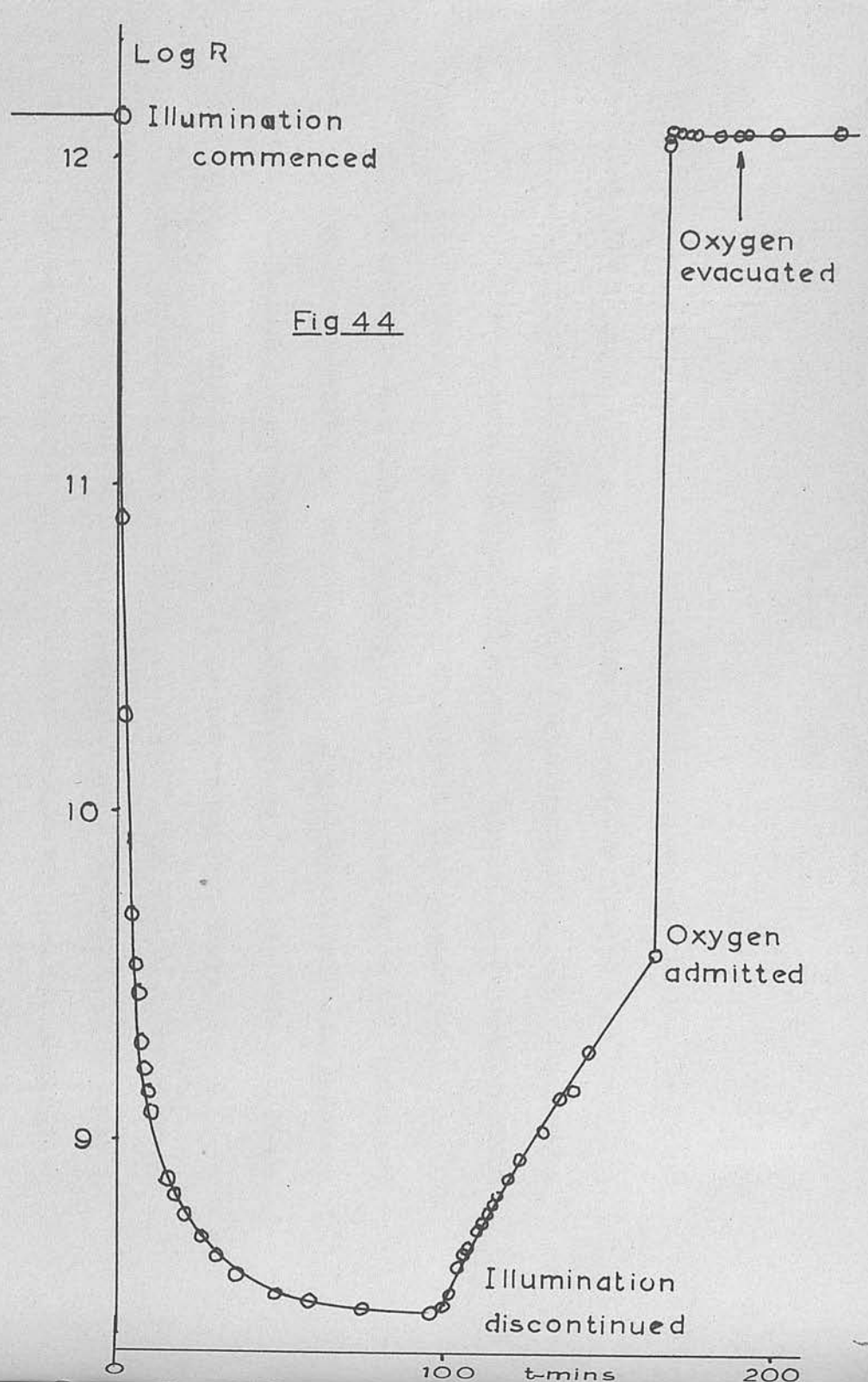
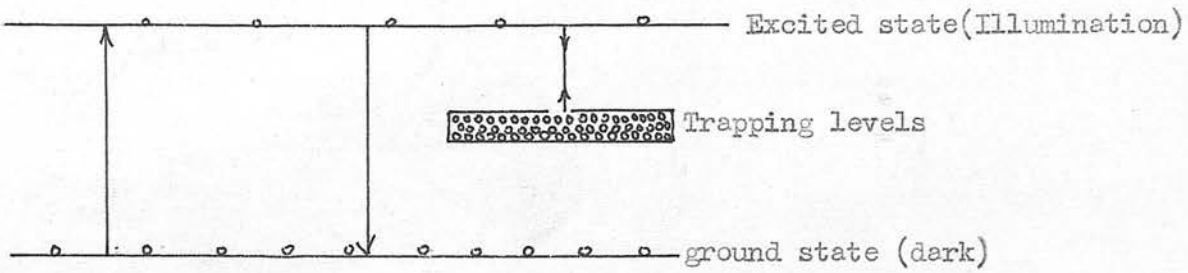

Log R
Illumination commenced
12
11
10
9
Oxygen evacuated
Oxygen admitted
Illumination discontinued
100
t-mins
200

Fig 44

excitation of the titanium dioxide by light absorption and resultant production of current carriers. On discontinuing the illumination the resistance increased at first quite rapidly and then later, quite slowly, the original resistance value was not attained for several days. Such a phenomenon could occur by processes involving various Trapping levels, as illustrated diagramatically here:-



Return from the trapping levels to the ground state would be accomplished thermally via the excited state.

Admission of oxygen (p_{O_2} = 147.5 mm.) during the decay of photo-conductivity caused an immediate return (Fig. 44) to the original resistance value before illumination, indicating that the current carriers in the trapping levels were being immobilised. Removal of the oxygen by evacuation did not cause any decrease in resistance and suggests that the removal of carriers was irreversible. With electrons as current carriers the following scheme is evisaged:-

1. Titanium dioxide + light $\longrightarrow$ $X^+ + e$
2. $O + e \longrightarrow O^-$
3. $O^- + X^+ \longrightarrow XO$

X^+ may be a proton as suggested by the production of water from films 1 and 2 (p. 41).

Photo/

Fig 45

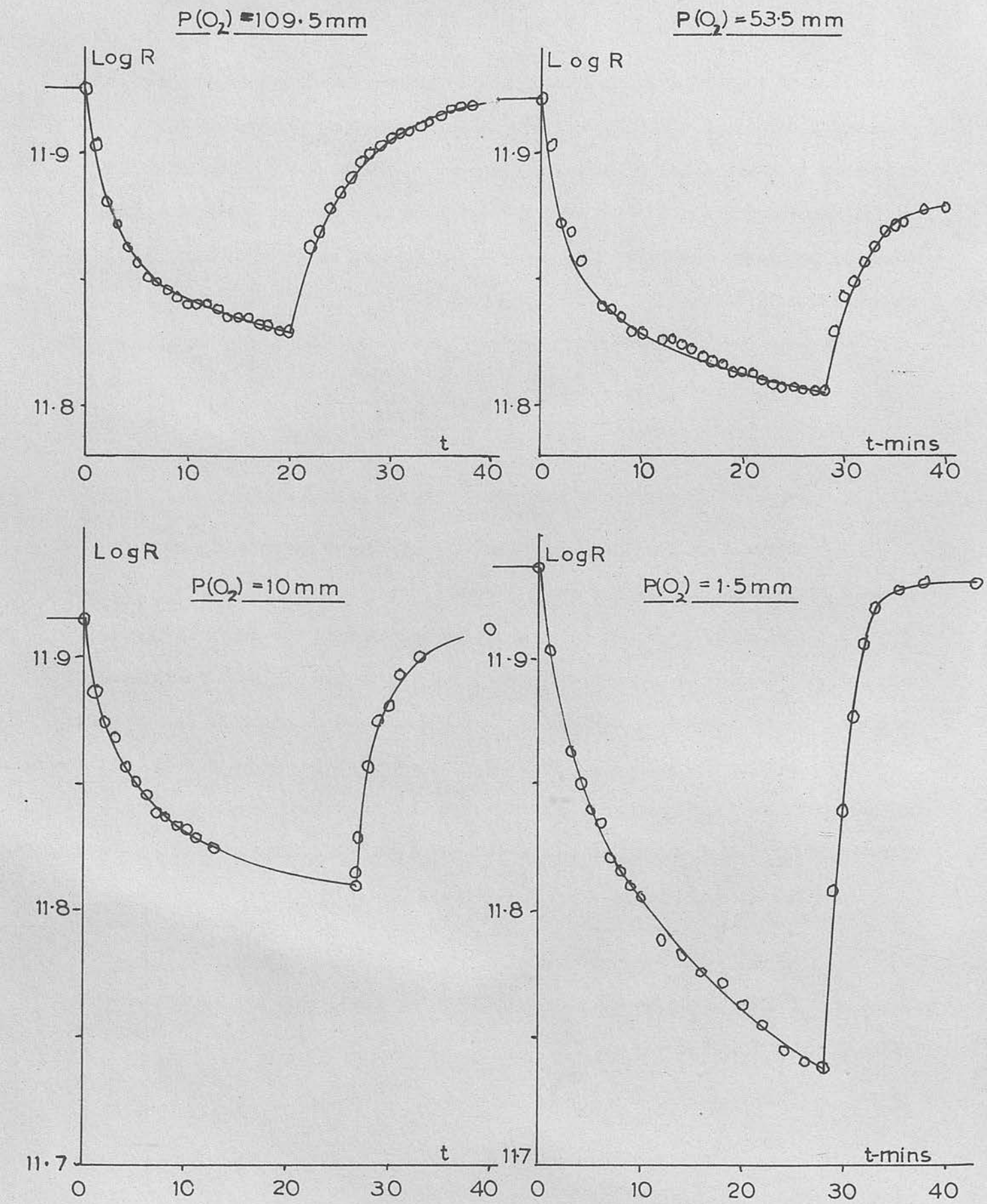

P(O2) =109·5mm
Log R
11·9
11·8
t
0
10
20
30
40
P(O2) =53·5 mm
L o g R
11·9
11·8
t-mins
0
10
20
30
40
LogR
P(O2) =10mm
11·9
11·8
11·7
t
0
10
20
30
40
LogR
P(O2) = 1·5mm
11·9
11·8
11·7
t-mins
0
10
20
30
40

Photo-conductivity in Presence of Oxygen.

In the presence of oxygen the photo-conductivity was very much suppressed (Fig. 45) and can be attributed to the constant removal of electrons from the trapping levels according to the schemes above. At oxygen pressures above 10 mm. the change in conductivity (Δ_{∞} log R) was reasonably constant:-

Table XLII

P_{O_2} mm.	Δ_{∞} log R (= log R$_{t=0}$ - log R$_{t=\infty}$)
109.5	0.100
53.5	0.118
10.0	0.108

and may be compared with Δ_{∞} log R for vacuum photoconductivity:-

Fig. 43 Δ_{∞} log R = 3.65
Fig. 44 Δ_{∞} log R = 3.62
(Traping levels full)

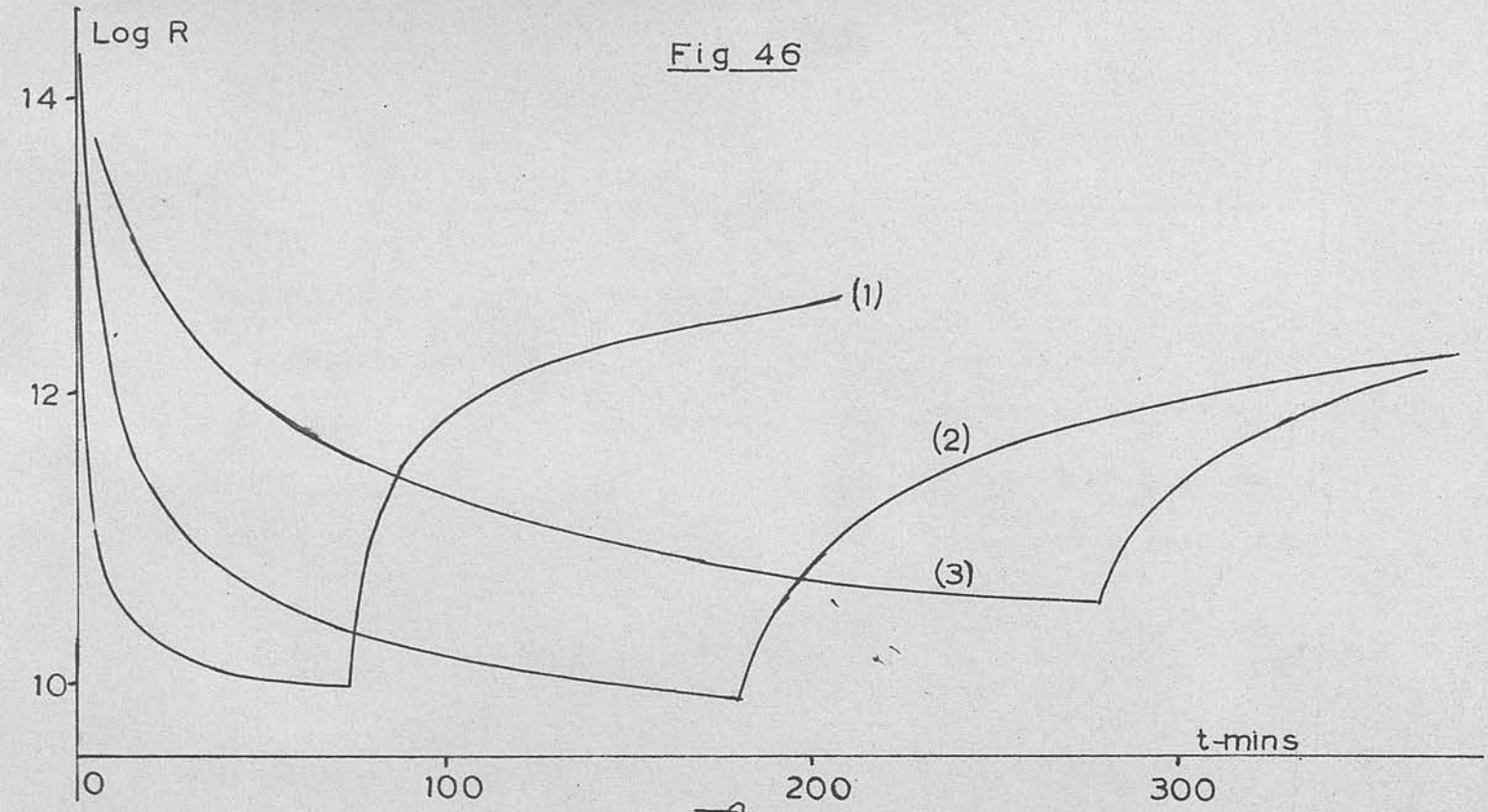
to show the rapid removal of carriers by oxygen.

For oxygen pressure below 10 mm. the extent of the photoconductivity increased; at P_{O_2} = 1.5 mm. the value of Δ_{∞} log R = 0.18 is in accordance with a lower surface concentration of adsorbed oxygen and a consequently lower rate of removal of electrons from the trapping levels. It is to be noted that the rate of restoration to the normal dark level was not so rapid even at the highest pressure of oxygen (Fig.45).

Effect of Oxygen Photo-uptake on Photo-Conductivity.

Measurement of the vacuum photo-conductivity of a bridge after photo-sorption of oxygen (Fig.46) showed the same general shape of the log R - t plots. The rate of attaining the minimum values of log R, however, was much /

Fig 46


Log R
14
12
10
(1)
(2)
(3)
t-mins
0
100
200
300

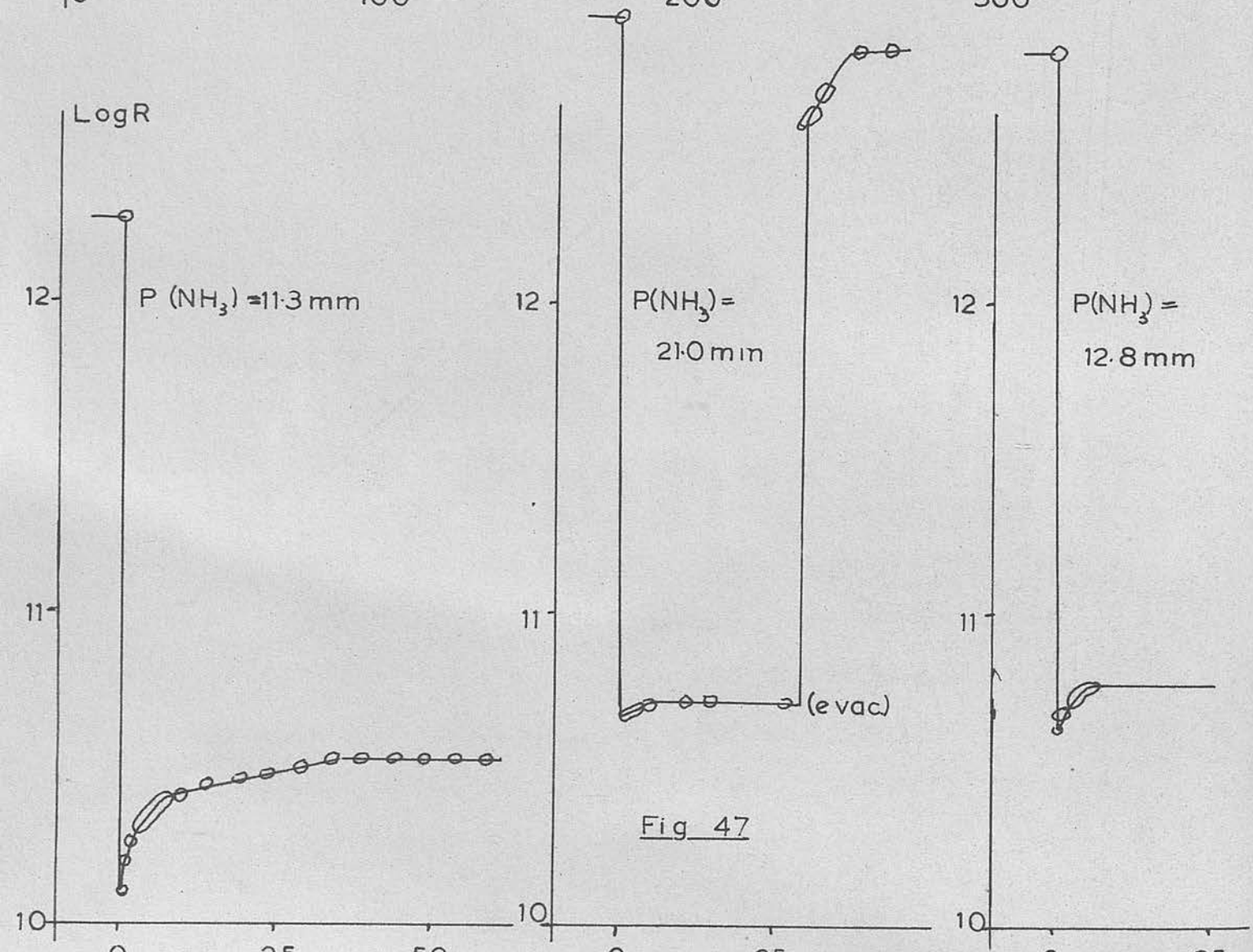

LogR
12
11
10
P (NH3) =11·3 mm
0
25
50
12
11
10
P(NH3)=
21·0 mm
(evac)
0
25
12
11
10
P(NH3) =
12·8 mm
0
25

Fig 47

Fig 48

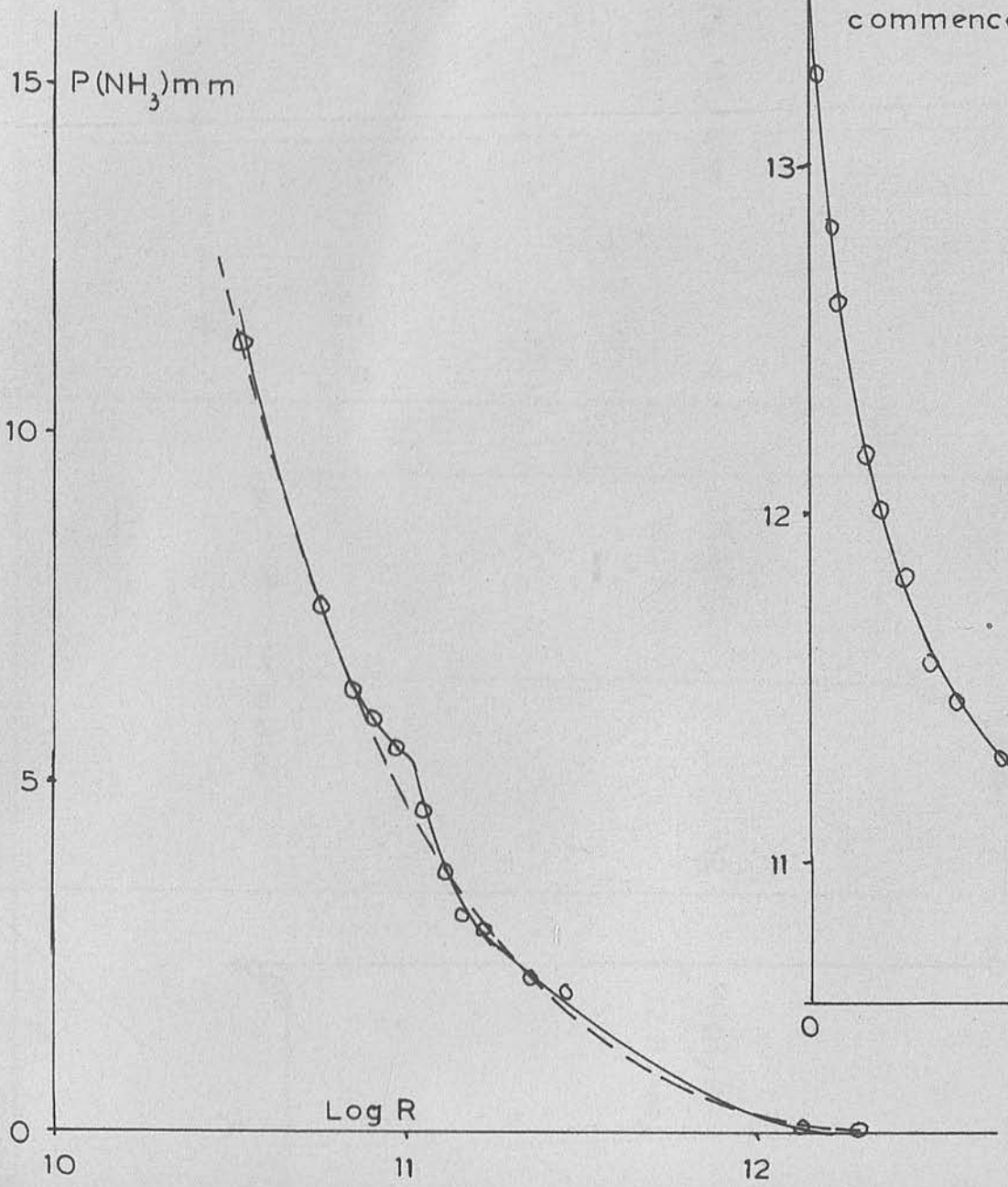
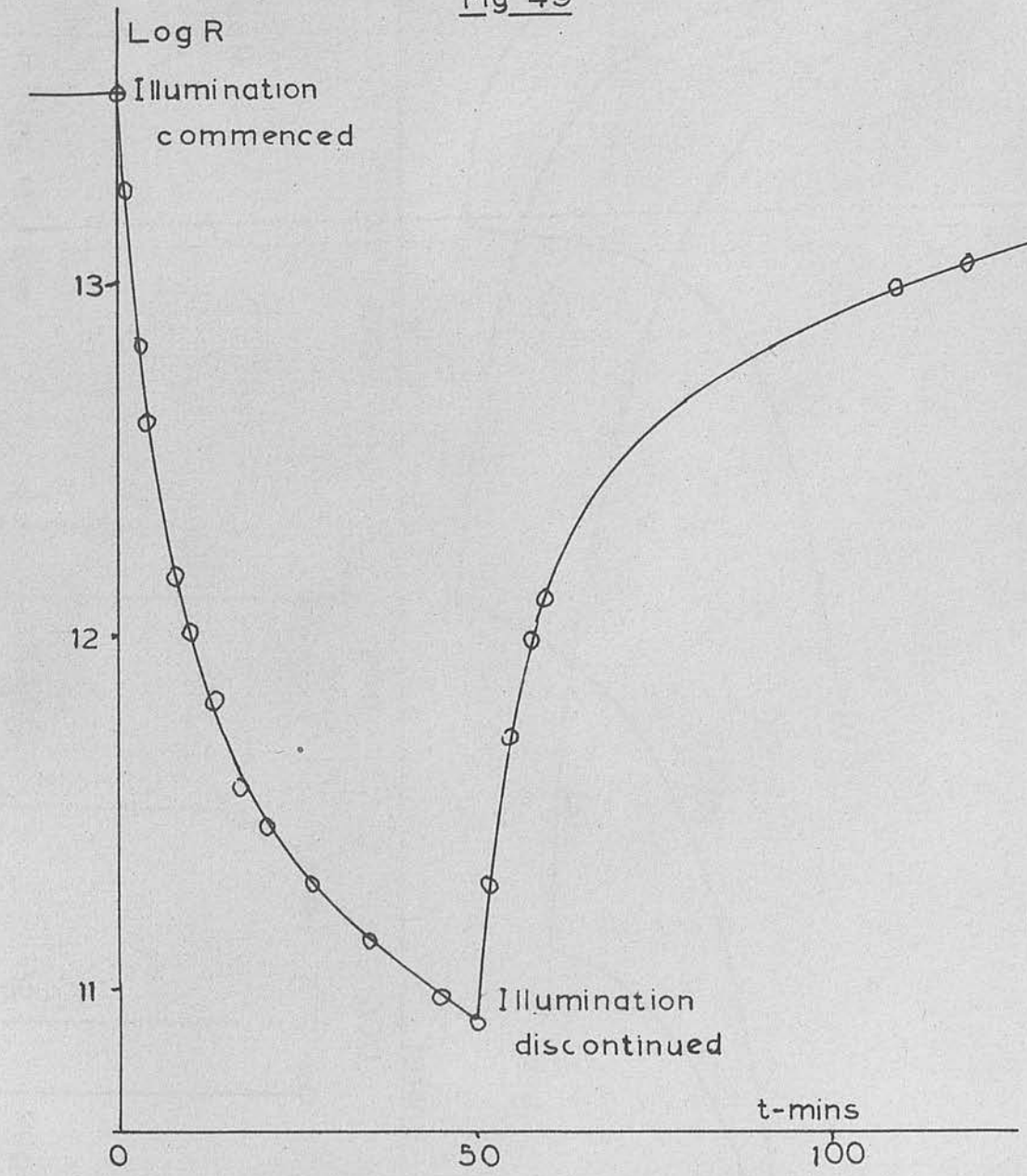

15
P(NH3)mm
10
5
0
Log R
10
11
12

Fig 49


Log R
Illumination
commenced
13
12
11
Illumination
discontinued
t-mins
0
50
100

much slower and in agreement with a depletion in the total number of carriers available due to oxygen photo-sorption. It would appear from this that the photo-uptake of oxygen is an irreversible process. Initial oxygen pressure $>$ 50 mm.

Fig. 46. (1) No oxygen photosorbed.

(2) Oxygen photosorbed for 72 mins.

(3) Oxygen photosorbed for further 130 mins.

Effect of Ammonia on Conductivity of Titanium Dioxide

The introduction of ammonia in the dark to an evacuated bridge of titanium dioxide caused an almost instantaneous decrease in resistance (Fig.47), followed by a small rapid increase, then a slow increase to a constant value. For three ammonia sorptions with evacuation between sorptions the values of the drops in resistance were $\Delta_{\infty} \log R = 1.74$, 2.10 and 2.01 for ambient ammonia pressures of 11.3, 21.0 and 12.8 mm. The rapid initial decrease in resistance must have been due to a condensation of ammonia on the surface and further resistance changes would have been associated with the subsequent water displacement raction.

Gradual removal of ammonia after the first admission caused the resistance to increase (Fig.48). (The possibility of a discontinuity at P_{NH_3} = 5 mm. was not established).

Vacuum Photo-conductivity after Ammonia Sorption.

In all respects the vacuum photoconductivity of ammonia treated titanium dioxide resembled that of untreated titanium dioxide (Fig. 49)

Replacement of water by ammonia does not inhibit photo-conductivity.

Photo-conductivity in an Ammonia Atmosphere

After the initial drop in resistance due to the addition of ammonia had /

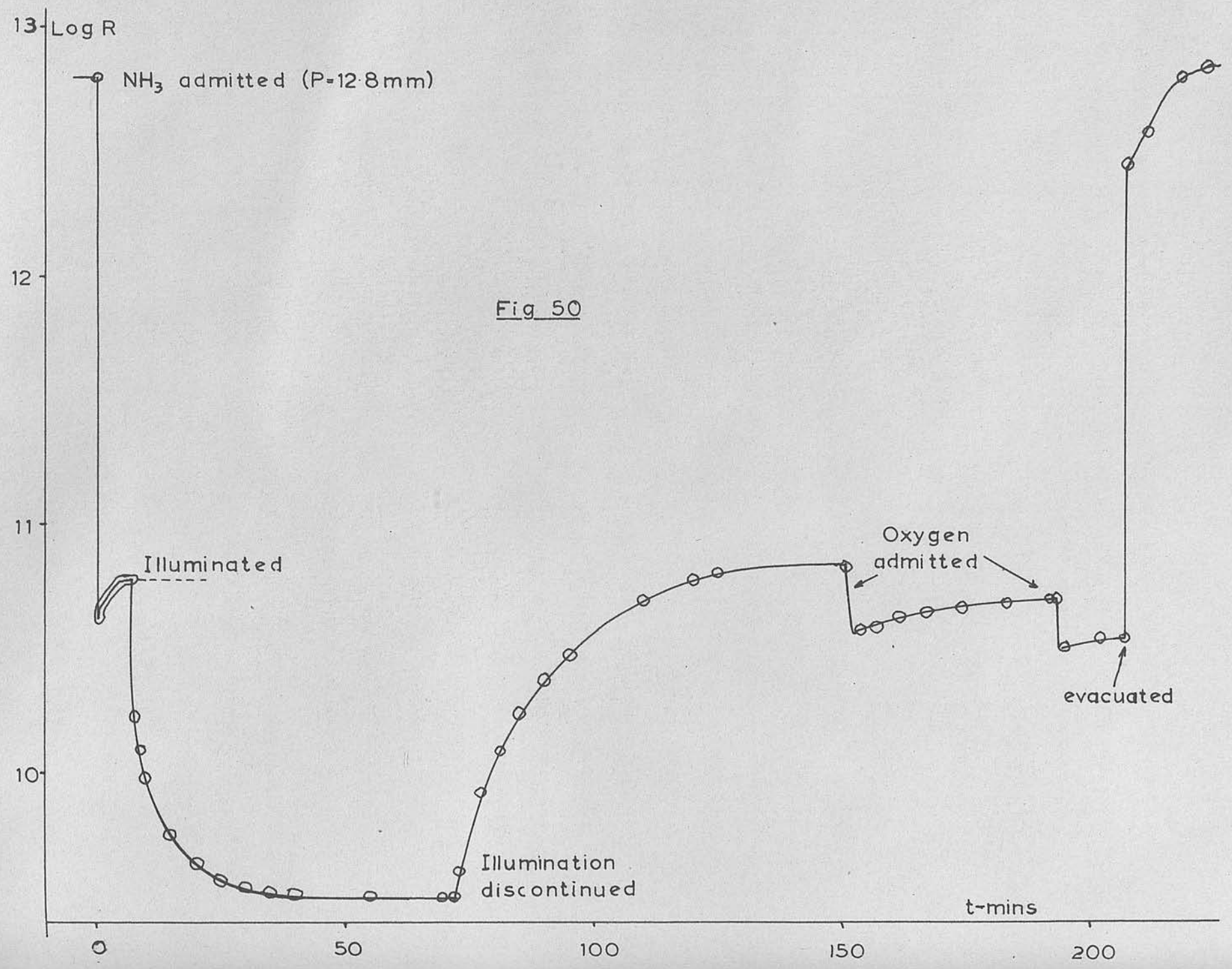

13
Log R
NH3 admitted (P=12·8mm)
12
11
10
Illuminated
Oxygen admitted
evacuated
Illumination discontinued
t-mins
0
50
100
150
200

Fig 50

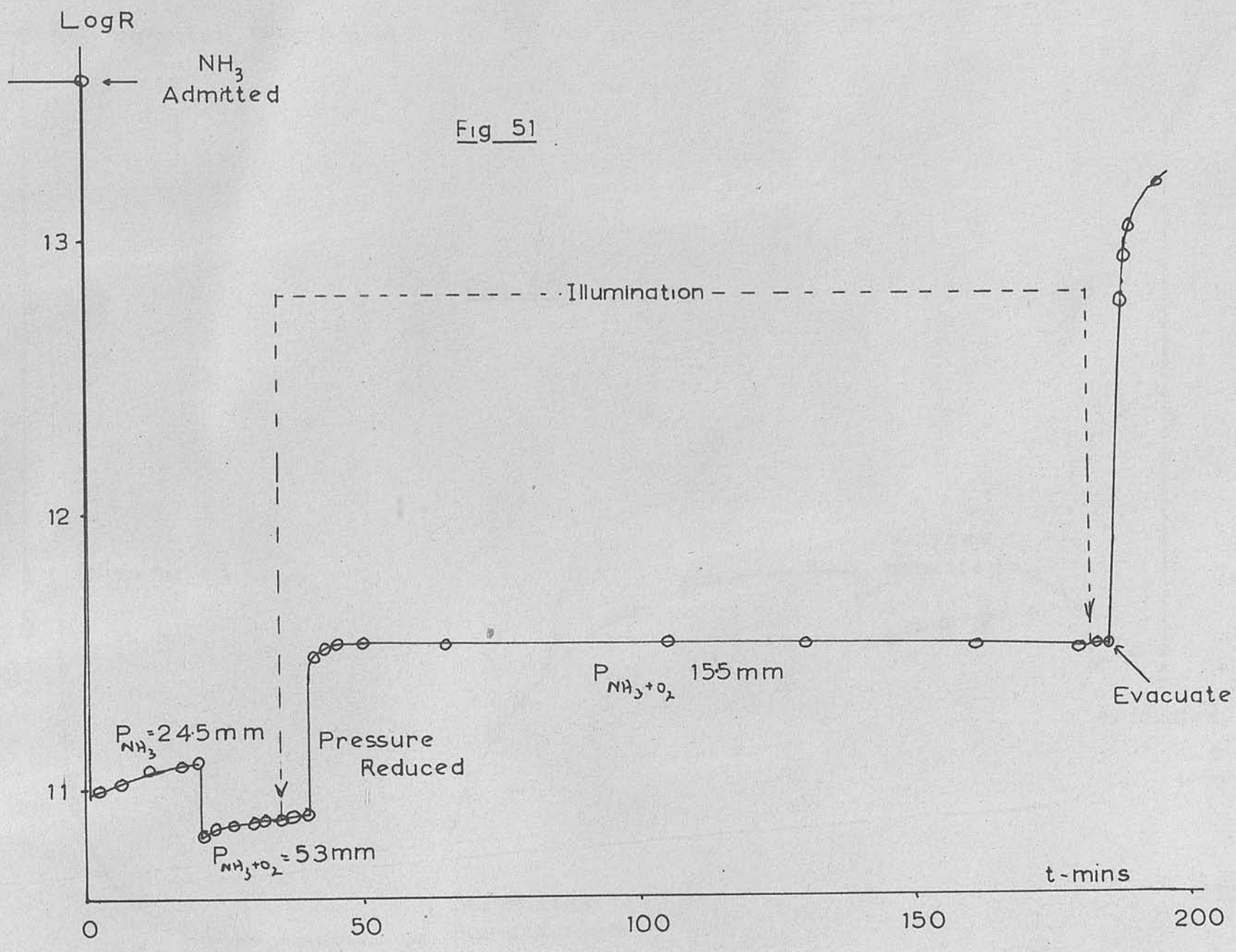

Log R
NH_3 Admitted
13
12
11
Illumination
$P_{NH_3+O_2}$ 155 mm
Evacuate
P_{NH_3} = 245 mm
Pressure Reduced
$P_{NH_3+O_2}$ = 53 mm
t - mins
0
50
100
150
200

Fig 51

had occurred and a steady resistance value was recorded illumination caused a further decrease in resistance (Fig.50):-

Δ_{∞}^{0}log R (thermal) = 2.01

Δ_{∞}^{0}log R (illumination) = 1.27

On discontinuing the illumination a rise in resistance occurred and the final value was approximately the same as that before illumination.

Addition of Oxygen to Ammonia Atmosphere

Addition of oxygen in the dark to an untreated bridge of titanium dioxide did not produce any measurable resistance changes. In the presence of ammonia, however, a decrease was observed, indicating a further condensation on the surface (Fig.50). In the photo-uptake of oxygen on an ammonia treated film (see page) the rate of oxygen uptake was a function of $\sqrt{\Delta p}$ i.e. $\sqrt{\Delta O_2}$, suggesting that there was a direct dissociative adsorption of oxygen on the surface. Ammonia has a lone pair of electrons and since the outer shell of oxygen has only six electrons it is possible that on the surface of titanium dioxide the further condensation may be due to oxygen giving a small equilibrium concentration of NH_3O.

$$NH_3 : + \ddot{O}: \rightleftharpoons NH_3 : \ddot{O}: \rightleftharpoons (NH_2^+ + OH^-)_{\text{etc.}}$$

The addition of oxygen did not cause any permanent change as was shown by the return to the original resistance on evacuation.

Action of Light in Presence of Ammonia and Oxygen.

No large changes in resistance occurred showing that the presence of oxygen was preventing the filling of trapping levels with electrons. Illumination for 150 mins. (Fig.51) did cause a small overall decrease in resistance /

resistance and might be attributed to the increase in the number of molecules adsorbed on the surface due to production of water by oxidation. Due to lack of confirmation, however, it must be admitted that the decrease may have been due to a gradual "drift" in the recordings.

SUMMARY

(1) The absorption of light energy resulted in the reduction of the resistance of titanium dioxide.

(2) The time dependance of the reduction in resistance may be attributed to a gradual filling up of trapping levels with electrons.

(3) Admission of oxygen in the dark to an evacuated sample of titanium dioxide did not give rise to any measurable changes in conductivity. It is to be concluded that the sorption of oxygen on the surface was very small at 20°C.

(4)The presence of oxygen during illumination tended to suppress photo-conductivity effects due to a continual removal of electrons from the trapping levels.

(5) Introduction of ammonia to an evacuated bridge resulted in the rapid decrease in resistance, due to adsorption on the surface of a layer of ammonia. Further changes (increase)in resistance may have been associated with the water displacement reaction.

(6) Displacement of water by ammonia did not appear to alter the vacuum photo-conductivity characteristics.

(7) /

(7) Excess ammonia did not cause any appreciable suppression in photo-conductivity. Ammonia cannot accommodate additional electrons as can oxygen.

(8) Addition of oxygen to an ammonia atmosphere caused a small reduction in the resistance and was in accordance with a further surface condensation. It may be that there was a small surface equilibrium concentration of associated ammonia and oxygen.

(9) Oxygen in the ammonia atmosphere prevented photo-conductivity effects, probably due to removal of electrons. Surface sorbed water produced by the photo-oxidation of ammonia may have caused a slow decrease in resistance.

DISCUSSION OF EXPERIMENTAL RESULTS

Early work by Jacobsen (1), Renz (6), Weyl and Forland(10) and Goodeve (11) was interpreted to mean that the illumination of titanium dioxide produced oxygen for oxidation purposes. On the other hand, however, Ruben (7) and Goetz and Inn (8) suggested by their results that the titanium dioxide was being oxidised. It was not until Mackenzie (12) showed titanium dioxide to photosorbed oxygen that any real advance in the problem has been made. Further work by Kennedy (13) uncovered many more facts concerning the oxygen uptake and also showed that a photo-uptake of nitric oxide occurred to give N_2O. This was the first mention of any products accompanying photo-reactions with single gases and titanium dioxide.

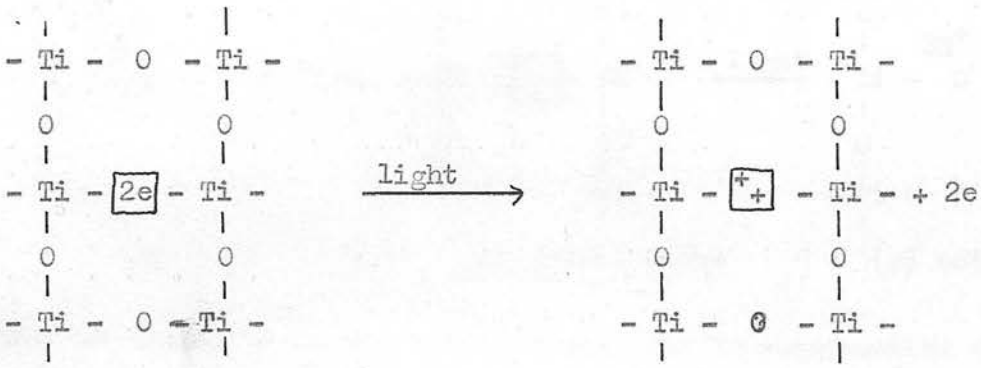
The preceding experimental sections have shown that various gases (O_2, NO and NH_3) have been adsorbed or photo-sorbed on titanium dioxide. Evacuation of the samples did not result in a complete recovery of all reactants and the presence of products in simple quantitative proportion to the amount of non-recovered reactant suggested that a definite chemical reaction was occuring. The relatively mild treatment required to recover some products indicated that the reaction was occurring on the surface. Except for the photo-oxidation of ammonia these reactions occurred to an extent that was limited and which could be determined by extrapolating to zero rate of reaction. The extrapolated values were such that it appeared there were a specific number of "sites" on the surface. For a given reaction each site was assumed to undergo the same reaction and gave the same products; a different reactant gave different products. Pretreatment of the titanium dioxide, i.e. with acetone, methyl-ethyl ketone or ammonia caused an alteration in the subsequent oxygen uptake under illumination. The sites /

sites were theremally activated in the case of ammonia-water displacement and photo-activated with light of a wavelength less than 4410Å for oxygen and nitric oxide uptakes. An increase in conductivity was observed on illumination thus classifying the titanium dioxide as a semiconductor. In short, the problem investigated was one of chemisorption and oxidation on a light activated semiconductor.

Impurity centres in Titanium dioxide.

The various types of semiconductors have already been dealt with in the introduction. Under the action of light the large time dependant decrease in resistance of titanium dioxide must have been due to the production of mobile current carriers. The introduction of oxygen during these measurements always succeeded in suppressing the conductivity. In some way these current carriers were immobilised by oxygen. It was not possible to inhibit completely by this method changes in conductivity on illumination. On the assumption that photoconductivity could arise from the mobilisation of electrons trapped in oxygen ion vacancies (Schottky Defects) within the lattice the following could occur:-

(1)



resulting /

resulting in the production of +ve holes (immobile) and electrons (mobile) Oxygen uptake would then follow:-

(2) $O + 2e \longrightarrow O^{--}$

(3) $O^{--} + \boxed{{}^{+}_{+}} \longrightarrow O$

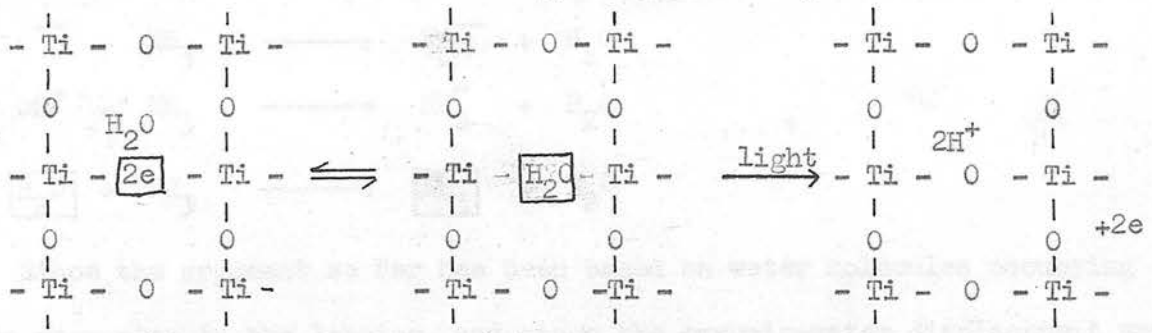
causing the oxygen ion vacancy to be filled. Unfortunately, this simple scheme does not explain why the uptake of oxygen was accompanied by the production of water. It also suggests that in the presence of hydrogen the positive holes may react with hydrogen to give protons:-

(4) $\boxed{{}^{+}_{+}} + H_2 \longrightarrow 2e + 2H^+$

Such a scheme would result in the production of water from an oxygen-hydrogen gas phase and give rise to a greater extrapolated value for the photo-uptake.

Experiment has shown that the extrapolated photo-uptakes from atmospheres of oxygen and oxygen + hydrogen were both the same and therefore in disagreement with this theory. If, however, the oxygen ion vacancy was filled with an interstitial water molecule the possibility of oxygen uptake with water production becomes a little more in agreement with experiment:-

(5)



(a) (b) ground state (c) activated

The two electrons in the oxygen vacancy can be accommodated within the 3d levels of neighbouring titanium ions and the water molecule can occupy the /

the vacancy (a). Effectively this would be equivalent to a water molecule being placed between two trivalent titanium ions in the lattice (b). On absorption of light energy a transition would occur to give state (c) which has resulted through the elevation of the two electrons to a conduction band and the production of two protons (surface bound) to maintain electric neutrality. The production of water would then be a direct result from photosorption of oxygen:-

(6) $O_2 + 4e \longrightarrow 2\ O^{--}$ (2 sites required)

(7) $2\ O^{--} + 4H^{+} \longrightarrow 2\ H_2O$

---

(6) + (7) $O_2 + 4\ H^{+} + 4e \longrightarrow 2\ H_2O$

This agrees with experiment (see films 1 and 2) and would also be in agreement with the experimental fact that the photo-uptake from a hydrogen - oxygen mixture would be the same as that from oxygen alone.

It was found that one ammonia molecule reacted with titanium dioxide to produce one water molecule. This process could have arisen from three possible reactions:-

(8) $O^{--} + NH_3 \longrightarrow NH^{--} + H_2O$

(9) $OH^{-} + NH_3 \longrightarrow NH_2^{-} + H_2O$

(10) $\boxed{H_2O} + NH_3 \longrightarrow \boxed{NH_3} + H_2O$

Since the argument so far has been based on water molecules occupying oxygen ion vacancies in the lattice, and since the ammonia-water displacement was of the same order as the oxygen uptake, equation 10 appears to be the most probable reaction. Two intersititial water molecules would (i) result in uptake of /

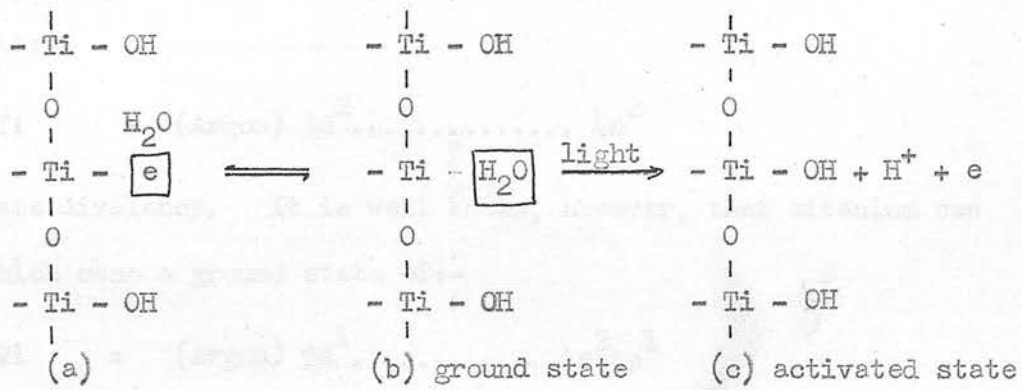
of one oxygen molecule and (ii) would exchange with two ammonia molecules. From this model system it is apparent that the extrapolated oxygen uptake ($\underset{\infty}{\Delta}O_2$) should be one half of the extrapolated ammonia uptake ($\underset{\infty}{\Delta}NH_3$). Experiment shows, however, that this is not so:-

$$\underset{\infty}{\Delta}O_2 = 1 \times 176 \ \mu/g. \quad \text{(film 2)}$$
$$= 1 \times 170 \ \mu/g. \quad \text{(film 3)}$$
$$\underset{\infty}{\Delta}NH_3 = 4 \times 164.5 \ \mu/g. \quad \text{(film 10)}$$
$$= 4 \times 160 \ \mu/g. \quad \text{(film 11)}$$

and $\underset{\infty}{\Delta}O_2 = \frac{1}{4} \underset{\infty}{\Delta}NH_3$. Photochemical activity resulting from states 5(a), 5 (b) and 5(c) above must be rejected on the grounds that it does not explain the quantitative results of films 2, 3, 10 and 11.

Earlier in the experimental section it was calculated that the water content of the titanium dioxide remaining after thorough evacuation was sufficient to provide a partial monolayer in the form of OH groups. While discarding the idea of oxygen ion vacancies in favour of hydroxyl ion vacancies and retaining the possibility of the existence of water molecules in these vacancies the following would represent schematically the postulated nature of an impurity centre:-

(11)



with /

with the electron in the OH-vacancy being accommodated within the 3d level of the neighbouring titanium ion when in the ground (or lowest energy) state (11b), i.e., in the dark. Activation by absorption of light energy would cause a transition to the state represented by 11 c. From this model it is seen that one oxygen molecule would abstract four electrons and four protons to form two water molecules from four "impurity centres". Four of these centres would exchange water for four ammonia molecules, and account for the values:-

$$\underset{\infty}{\Delta} O_2 = 1 \times 176 \; ; \quad 1 \times 170 \; \mu/g.$$

and

$$\underset{\infty}{\Delta} NH_3 = 4 \times 164.5 \; ; \; 4 \times 160 \; \mu/g.$$

The relatively larger value of $\underset{\infty}{\Delta} O_2$ might be attributed to a small amount of impurity centres of the type illustrated by 5 (b).

Lewis acids (46) which are found in silica-alumina catalysts, are very much akin in nature to the postulated impurity centre 11 b. Their occurrence is due to the known property of alluminium ions to accept a lone pair of electrons to fill the 3p atomic orbitals. The electronic ground state of aluminium is:-

$$Al = (Neon)\ 3s^2 3p^1$$

and for titanium is:-

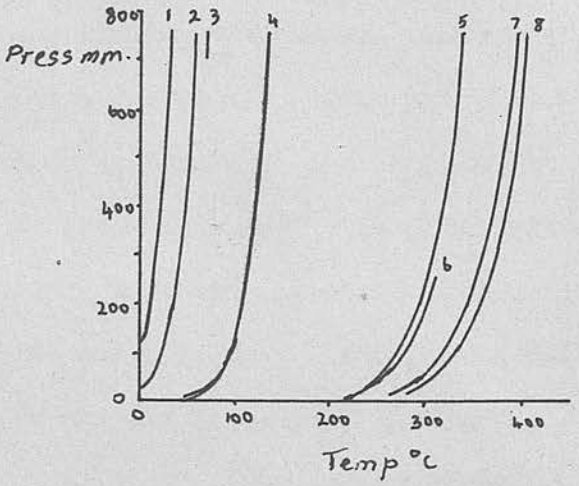
$$Ti = (Argon)\ 3d^2 \ldots\ldots\ldots\ldots\ 4s^2$$

which would indicate divalency. It is well known, however, that titanium can be trivalent in which case a ground state of:-

$$Ti = (Argon)\ 3d^1 \ldots\ldots\ldots\ 4s^2 4p^1$$

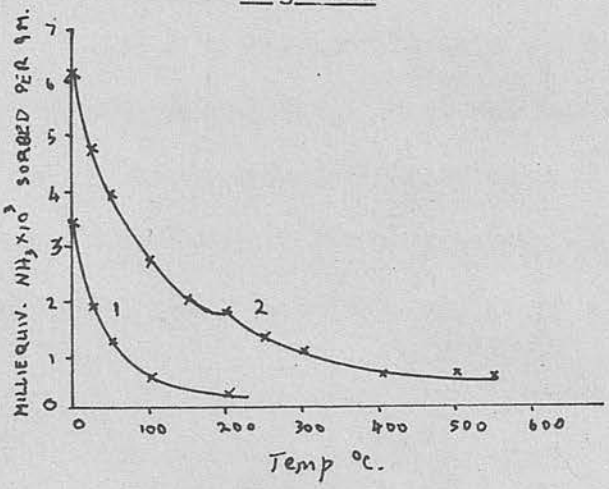
can exist. Very similar properties to aluminium salts would then be expected from /

Fig 41



1- NH_4SH, NH_4CN.
2- $NH_4CO_2NH_2$
3- $(NH_4)_2CO_3$
4- NH_4N_3
5- NH_4Cl.
6- $NH_4.HSO_4$
7- NH_4Br
8- NH_4I.

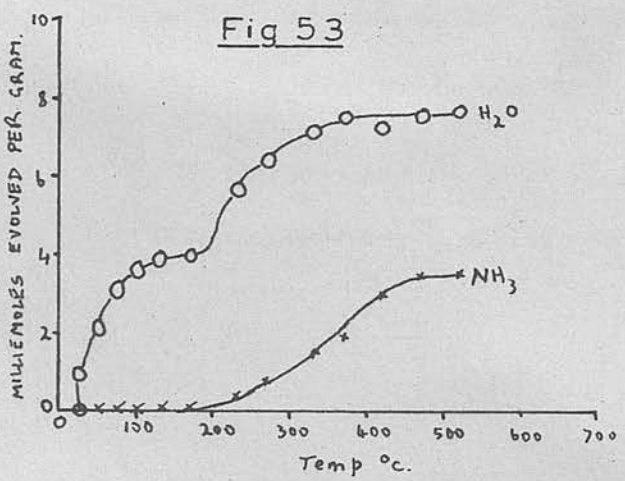
Fig 52



1- Silica gel
2- Silica-alumina catalyst

NH_3 Pressure = 7.5 cms Hg.

Fig 53



from trivalent titanium salts, e.g. $TiCl_3$ and $AlCl_3$ both form hydrates of the type $XCl_3.6H_2O$ and both form true alums of the type $KX(SO_4)_2.12H_2O$. The ground states of silicon and titanium (valency = 4) are respectively:-

$$Si = (Neon)\ 3s^2 3p^2$$

and

$$Ti = (Argon).....4s^2 4p^2 \quad (\text{vacant 3d orbital})$$

Silicon and tetravalent titanium both have similar properties in that they form liquid tetrachlorides which are easily hydrolysed into a hygroscopic gel with an indefinite water content.

Such similarities in chemical properties and electronic configuration would render feasible the production of a Lewis acid centre through the presence of a water molecule at a hydroxyl ion vacancy on the surface of titanium dioxide.

The presence of a proton at a Lewis acid centre gives rise to acidic properties. On studying the sorption of ammonia on a silica alumina catalyst Tamele (43) found that the phenomenon was a very complex one and probably involved physical sorption, chemisorption and capillary condensation. When compared with the sorption on silica gel (Fig.52) and equal surface area of silica-alumina gel retained more ammonia on heating. Fig.53 shows what happened when an ammonia treated silica gel catalyst was heated to 700°C. Up to 200°C water was evolved freely, at 200°C a further desorption of water occurred and was accompanied by desorption of ammonia. The second desorption of water was approximately equimolecularly equal to the ammonia desorption ($3.7\ H_2O$: $3.6\ NH_3$). Such a process could arise from the following:-

12) $-Al:O:H\ H^+ + NH_3 \xrightarrow{0-200^\circ C} -Al:O:H\ NH_4^+$

13) $-Al:O:H\ NH_4^+ \xrightarrow{200-500^\circ C} -Al:NH_2:\ H^+ + H_2O,$

14) $-Al:NH_2:\ H^+ \xrightarrow{200-500^\circ C} -Al + NH_3$

Support /

Support for this mechanism arises from the infra-red studies (Mapes and Eischans 47), of chemisorbed ammonia on silicia-alumina catalysts heated to 500°C where bands corresponding to NH_3 and NH_4^+ were identified in the absorption spectrum. If the processes given by 12,13 and 14 are to apply to ammonia and titanium dioxide it is at once apparent that the impurity centres or Lewis acids are thermally less stable:-

(15) $$-\overset{|}{\underset{|}{Ti}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H\ H^+ + NH_3 \xrightarrow{25^\circ C} -\overset{|}{\underset{|}{Ti}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H\ NH_4^+$$

(16) $$-\overset{|}{\underset{|}{Ti}} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} : H\ NH_4^+ \xrightarrow{25^\circ C} -\overset{|}{\underset{|}{Ti}} : \overset{\cdot\cdot}{NH_2} : H^+ + H_2O$$

(17) $$-\overset{|}{\underset{|}{Ti}} : \overset{\cdot\cdot}{NH_2} : H^+ \xrightarrow{>25^\circ C} -\overset{|}{\underset{|}{Ti}} + NH_3.$$

Information as to the occurrence of reaction 17 is lacking. It did not occur at 25°C.

The postulated Lewis acid type centres then account quantitatively for the oxygen photo-uptake and the ammonia-water thermal displacement.

Before extending the discussion to the photo-uptake of oxygen on acetone and methyl-ethyl ketone bound films, the photo-uptake of nitric oxide and the oxidation of ammonia, a survey of the extrapolated uptakes/gm. will give an indication of the likelihood of the other results being explained by the existence of Lewis acid type impurity centres.

TABLE XLIII /

TABLE XLIII

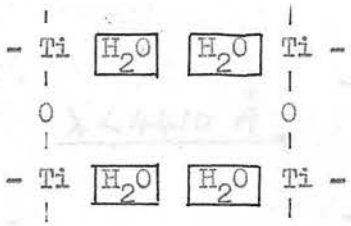
Process	Reactant
Oxygen photo-uptake	
(a) Water bound films (2,3)	$\Delta_{\infty} O_2 = 1 \times 173 \mu/gm.$
(b) Acetone bound films (4,5,6)	$\Delta_{\infty} O_2 = 3\frac{1}{2} \times 171 \mu/gm.$
(c) Methyl-ethyl ketone bound film (7)	$\Delta_{\infty} O_2 = 5 \times 171 \mu/gm.$
Nitric oxide photo-uptake	
(d) Water bound film (8)	$\Delta_{\infty} NO = 6 \times 171 \mu/gm$
Ammonia uptake	
(e) Water bound films (10,11)	$\Delta_{\infty} NH_3 = 4 \times 162 \mu/gm.$
(f) Oxygen photo-uptake on ammonia treated firlm (11)	$\Delta_{\infty} O_2 = 6 \times 162 \mu/gm.$
(g) Complex formation for photo-catalytic oxidation of NH_3 (15)	$\Delta O_2 = 2\frac{1}{2} \times 176 \mu/gm.$
	$\Delta NH_3 = 2 \times 183 \mu/gm.$
	$\Delta H_2O = 4 \times 186 \mu/gm.$

The above table shows how the extrapolated uptakes for various surface processes occurring on the titanium dioxide can be expressed as an integral multiple of $170 \mu/gm.$ If this value be taken as the actual number of sites the ammonia-water exchange experiments indicate that one site must contain four Lewis acid type impurity centres.

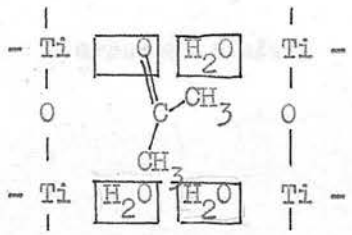
With regard to the increase in oxygen uptake of acetone and methyl-ethyl ketone bound films and to the formation of a complex in the catalytic oxidation of ammonia which would be reactions occurring over 4 impurity centres, a geometrical factor must be introduced. In the case of films 4, 5, 6 and 7 the increase in oxygen uptake with CO_2 and H_2O production could have been due to the oxidation of an acetone or methyl-ethyl ketone molecule chemisorbed on one impurity /

impurity centre and "spread over" a further three, thus inhibiting further chemisorption, by steric hindrance, on the site. This and the complex formation of film 15 suggests that the four impurity centres be in close proximity with each other:-

i.e. (18)



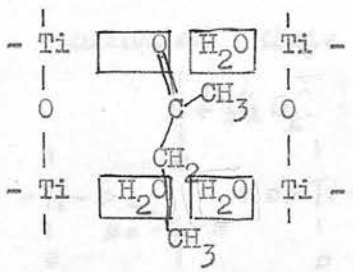
acetone



(18a)

chemisorbed acetone molecule on site (ground state)

methyl-ethyl ketone



(18b)

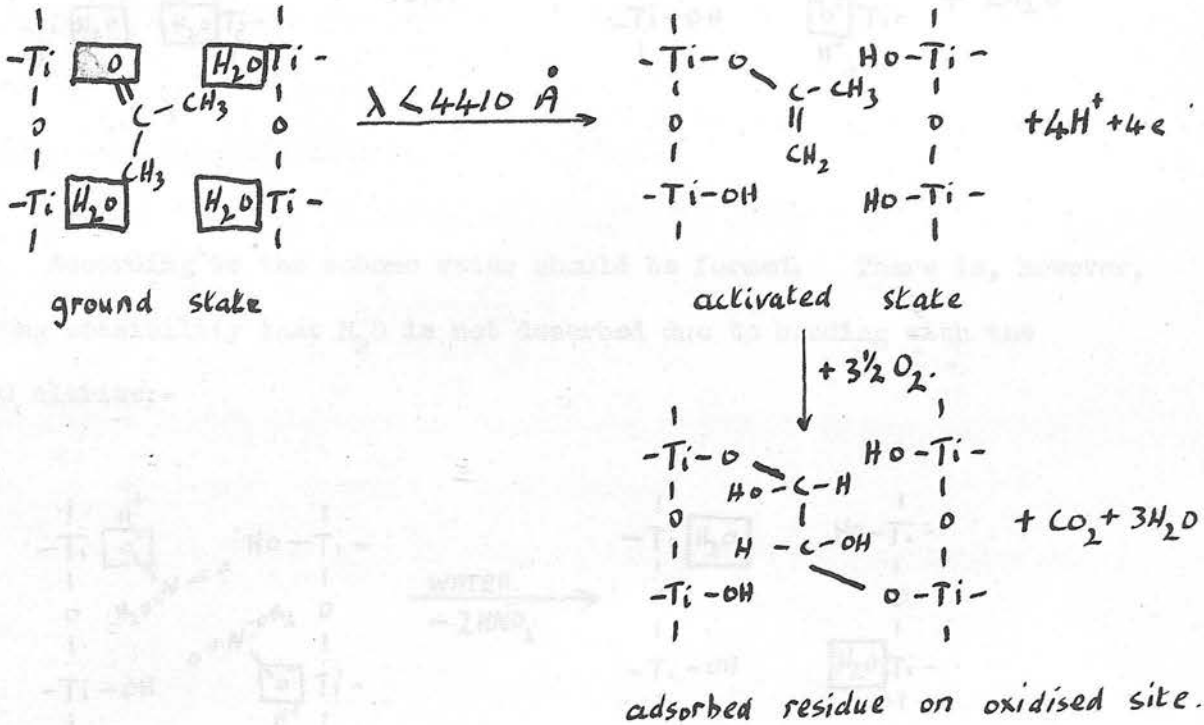
chemisorbed methyl-ethyl ketone molecule on site (ground state)

The sorption of acetone and methyl-ethyl ketone would be accompanied with the expulsion of a water molecule from each site. This was not verified experimentally. Such an arrangement as (18) would perhaps occur along lattice dislocations where they emerge on the surface. Possible schemes in agreement with experimental results are given below:-

(a) Oxidation of chemisorbed acetone:- /

(a) Oxidation of chemisorbed acetone:-

(18a)



(b) Methyl-ethyl ketone bound film

(18b)

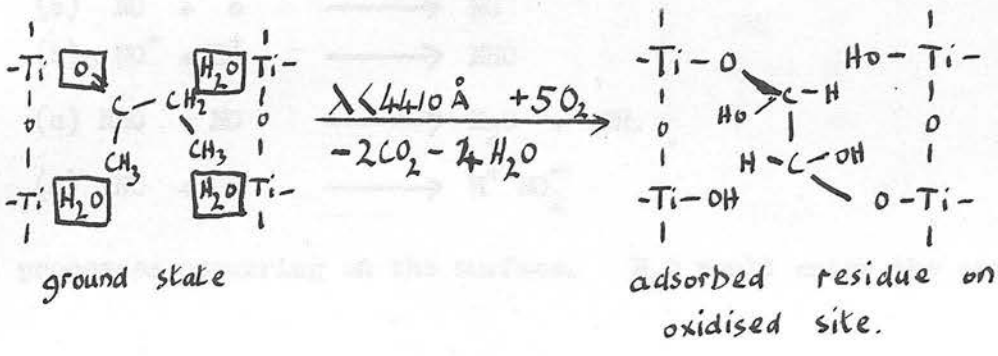
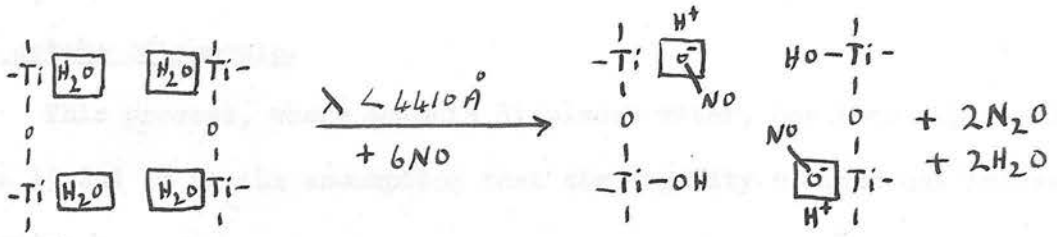
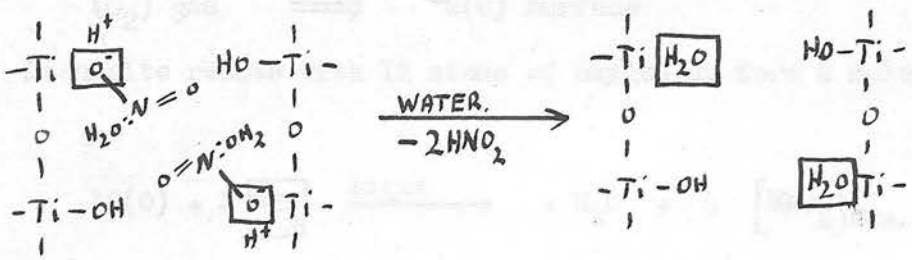


Photo /

Photo uptake of nitric oxide

(19) 

According to the scheme water should be formed. There is, however, the strong possibility that H_2O is not desorbed due to bonding with the adsorbed nitrite:-

(19a) 

The experimental yield of water was only 30% of that predicted by equation 19. Exchange of the adsorbed nitrite with water was easily accomplished indicating a weak surface bonding of the type illustrated above. The mechanism of the reaction producing N_2O and NO_2^- may be as follows:-

(a) $NO + e \longrightarrow NO^-$

(b) $NO^- + H^+ \longrightarrow NHO$

(c) $NHO + NO \longrightarrow N_2O + OH.$

(d) $NO + OH \longrightarrow H^+ NO_2^-$

with all processes occurring on the surface. N_2O would enter the gas phase since /

since it does not convert to ionic forms by accepting or donating electrons, as does NO and OH.

Thermal uptake of ammonia.

This process, where ammonia displaces water, has been explained by equation 15 and 16 on the assumption that the impurity centres can behave like Lewis acids.

Oxidation of Chemisorbed Ammonia.

The kinetics of the uptake of oxygen on film 11:-

$$\frac{d\Delta O_2}{dt} = K\left(\frac{\sqrt{\Delta_\infty O_2} - \sqrt{\Delta O_2}}{\sqrt{\Delta O_2}}\right)$$

would suggest a direct dissociative adsorption of oxygen on the surface:-

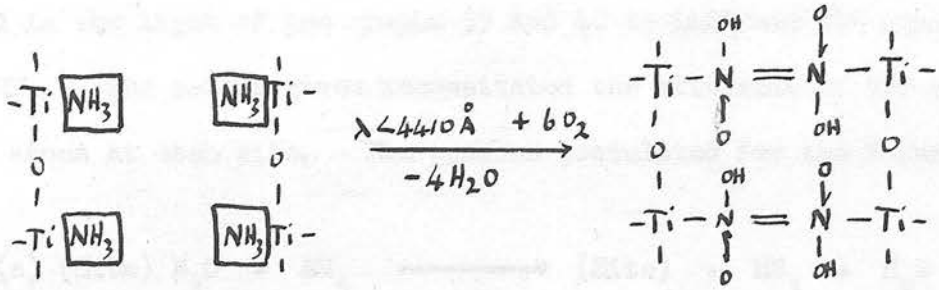
$$(O_2)\ \text{gas} \rightleftharpoons 2(O)\ \text{surface}$$

Each site reacts with 12 atoms of oxygen to form 4 molecules of water:-

$$12(O) + 4\,[NH_3] \xrightarrow{\text{light}} 4\,H_2O + 4\,[HNO_2]_{ads.}$$

The residue was not extracted in the form of nitrite by water and therefore the adsorbed residue was not the same as was found on the uptake of nitric oxide:-

(20)



20 a.

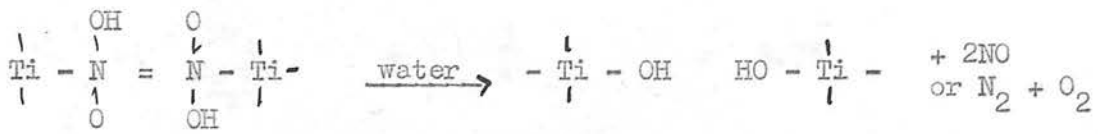
(20a would be a possible explanation as to the structure of the adsorbed residue.

An/

An incomplete uptake of oxygen could result in the production of N_2O:-

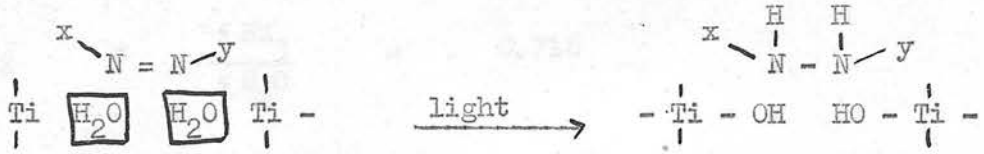
(20b) 

Extraction of the illuminated film with water would yield NO or O_2 and N_2

(20c) 

Further reaction of NO with dissolved oxygen in the water could yield traces of nitrite.

Such a structure as described by (20a) would render feasible the suggestion in the introduction that chlorazol sky blue sorbed on the surface of titanium dioxide may be reduced when illuminated in vacuo i.e.

(21) 

Complex formation with Subsequent Oxidation of Ammonia to Nitrous Oxide and Hydrazoic Acid

The build up of a complex for the oxidation of ammonia was shortly discussed in the light of the graphs 39 and 40 to indicate the production of N_2O and HN_3. The scheme given necessitated the existence of two oxidisable hydrogen atoms at each site. The process postulated for the formation of HN_3 was:-

(22) (a) (Site). N_2O + NH_3 ⟶ (Site) + HN_3 + H_2O

(b) (Site) + 2 NH_3 ⟶ (Site) . 2 NH_3

(c) (Site). 2 NH_3 + 2 O_2 ⟶ (Site). N_2O + 3 H_2O

(d) 3 NH_3 + 2 O_2 ⟶ HN_3 + 4 H_2O

The/

The ratios of reactants and products for this equation are:-

$$a_1 = \frac{NH_3}{O_2} = \frac{3}{2} = 1.50$$

$$b_1 = \frac{H_2O}{O_2} = \frac{4}{2} = 2.00$$

$$c_1 = \frac{NH_3}{H_2O} = \frac{3}{4} = 0.75$$

and the slopes given by figs. 39 and 40 give these ratios as:-

$$a_2 = \frac{\Sigma NH_3}{\Sigma O_2} = 1.36$$

$$b_2 = \frac{\Sigma H_2O}{\Sigma O_2} = 1.86$$

$$c_2 = \frac{\Sigma NH_3}{\Sigma H_2O} = 0.716$$

are low indicating that oxygen and ammonia have been used up in the formation of N_2O. O_2, NH_3 and H_2O are therefore each composed of two separate amounts, one for HN_3 production and the other for N_2O production

$$a_2 = \frac{\Sigma NH_3}{\Sigma O_2} = \frac{(NH_3)_A + (NH_3)_B}{(O_2)_A + (O_2)_B} = 1.36$$

$$b_2 = \frac{\Sigma H_2O}{\Sigma O_2} = \frac{(H_2O)_A + (H_2O)_B}{(O_2)_A + (O_2)_B} = 1.86$$

$$c_2 = \frac{\Sigma NH_3}{\Sigma H_2O} = \frac{(NH_3)_A + (NH_3)_B}{(H_2O)_A + (H_2O)_B} = 0.816$$

The ratios of:-

$$\frac{(NH_3)_A}{(O_2)_A} = \frac{3}{2} = a_1$$

$$\frac{(H_2O)_A}{} = /$$

$$\frac{(H_2O)_A}{(O_2)_A} = \frac{4}{2} = b_1$$

$$\frac{(NH_3)_A}{(H_2O)_A} = \frac{3}{4} = c_1$$

represent the formation of HN_3 by the equation (22d):-

$$2\,O_2 + 3\,NH_3 \longrightarrow HN_3 + 4\,H_2O$$

By simple algebra the ratios:-

$$\frac{(NH_3)_B}{(O_2)_B} = \frac{4}{3}$$

$$\frac{(H_2O)_B}{(O_2)_B} = \frac{5}{3}$$

$$\frac{(NH_3)_B}{(H_2O)_B} = \frac{4}{5}$$

then represent the formation of N_2O:-

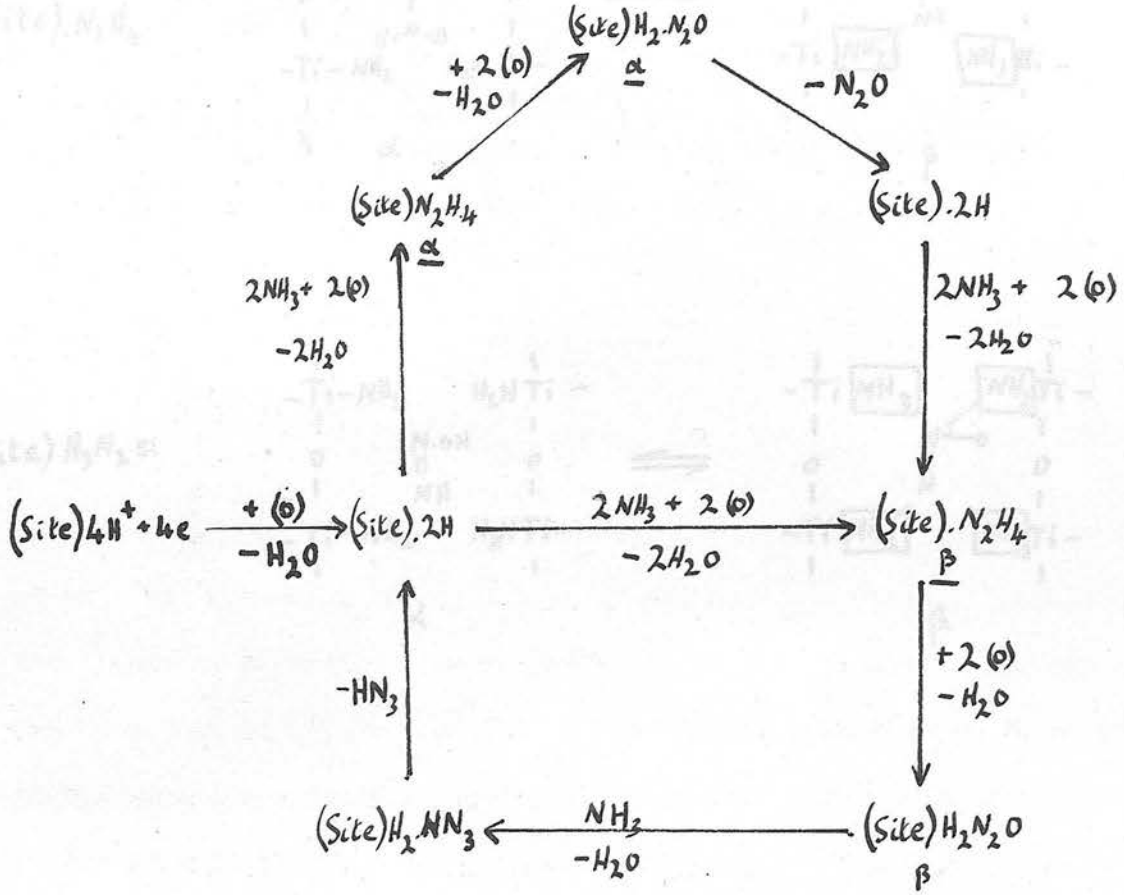
(23) $X + 3\,O_2 + 4\,NH_3 \longrightarrow (X + N_2H_2O) + N_2O + 5\,H_2O$

which is not a cyclic process.

(The ratio $\frac{\Sigma N_2O}{\Sigma H_2O} = 0.041$ and the ratio $\frac{\Sigma N_2O}{\Sigma O_2} = 0.069$ from Fig.40 gives

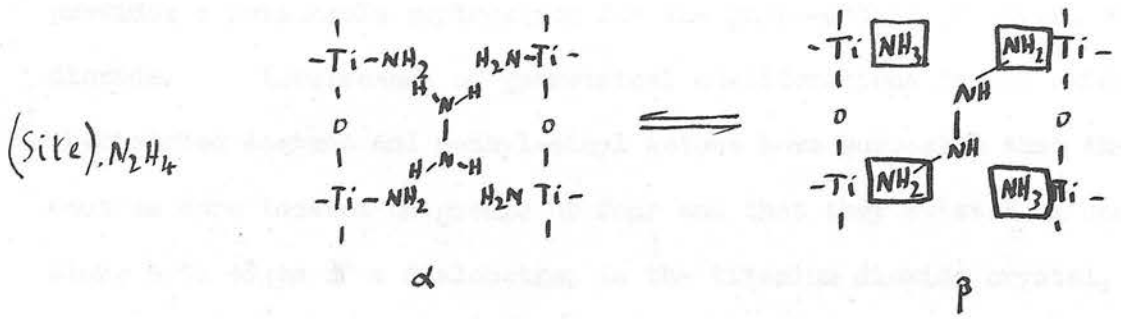
$\frac{\Sigma H_2O}{\Sigma O_2} = \frac{5.05}{3.00}$ supporting equation 23.) The production of N_2O however, occurred after the uptake of $2\frac{1}{2}$ O_2 and 2 NH_3 and must therefore represent an intermediate stage in the process represented by equation 23. Two processes then occurring on the complex, built up on one site, can be explained by the following /

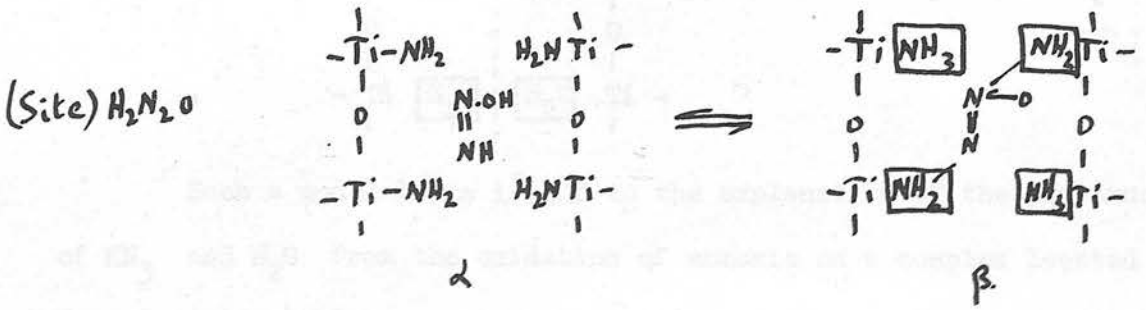
following diagramatic scheme:-



The important point about this scheme is the oxidation of (Site) N_2H_4 to (Site) H_2N_2O which either decomposes, (α form) to give N_2O or condenses with NH_3 to give HN_3 (β form). The following intermediate stages can be represented /

represented as resonating structures:-





The oxidation of ammonia would seem to depend upon the ability of the ammonia substituted site to act as a proton donator and acceptor:-

The /

Fig 54

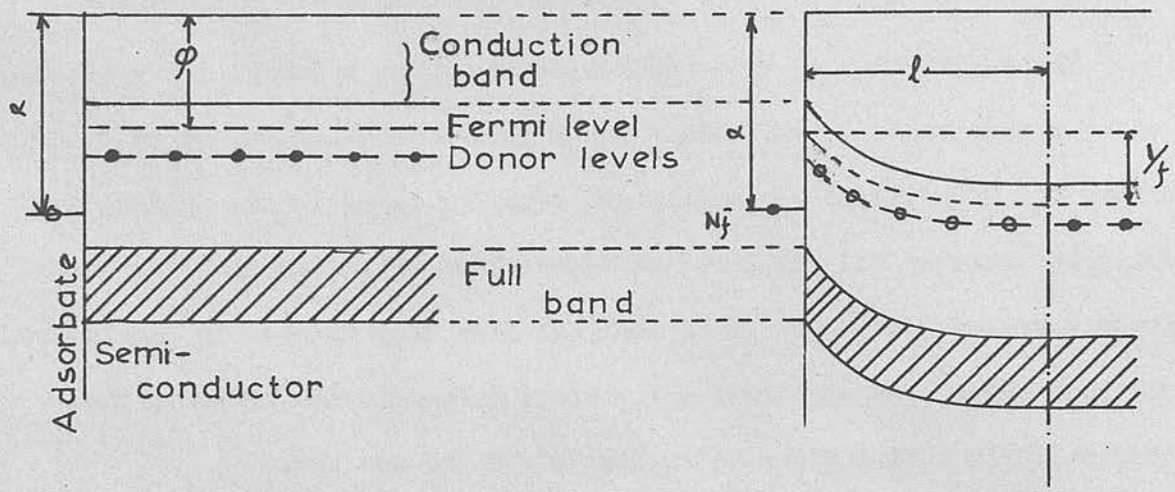
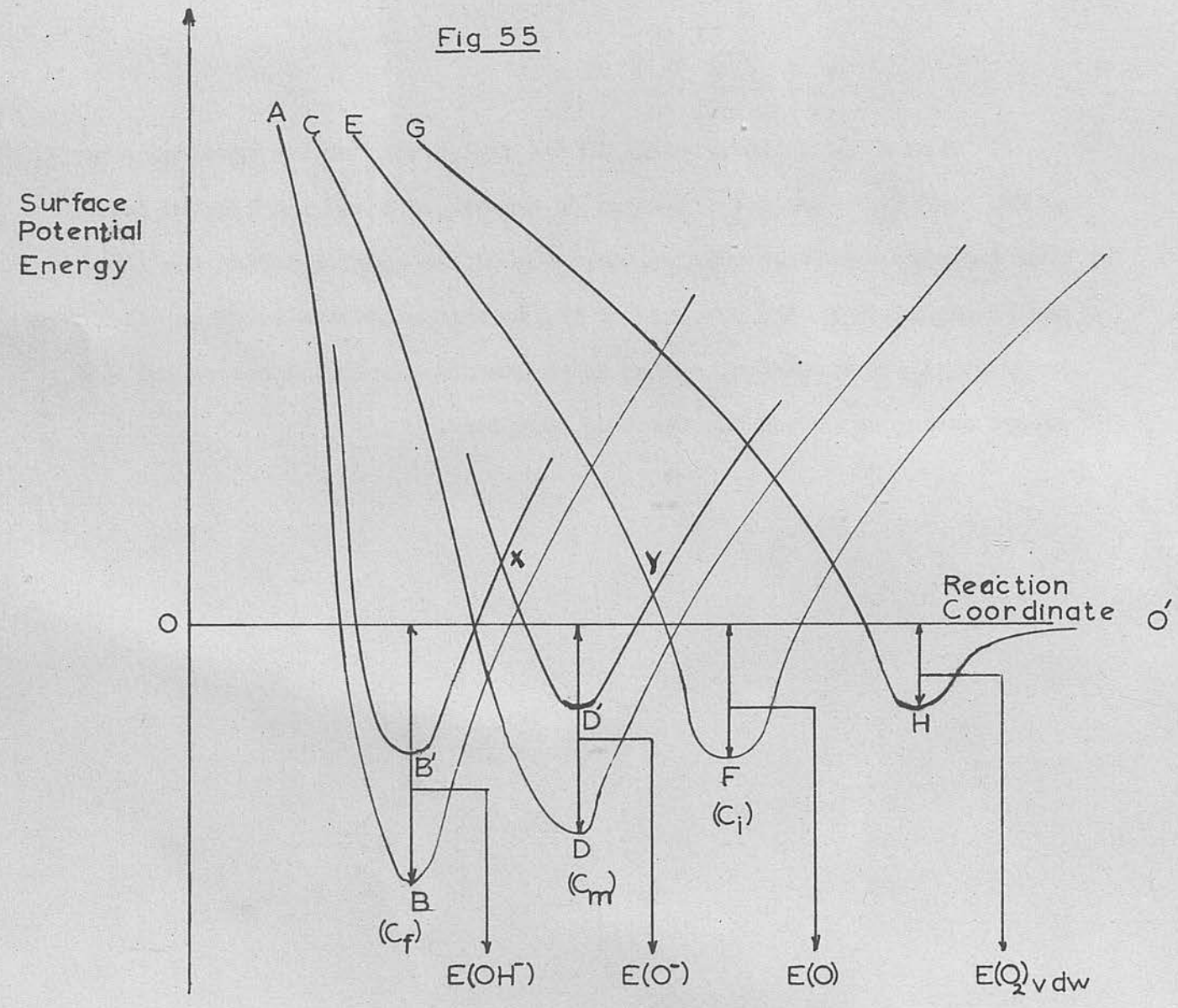

Conduction band
Fermi level
Donor levels
Full band
Adsorbate
Semi-conductor
χ
φ
α
l
Y/f
Nf

Fig 55


Surface Potential Energy
A
C
E
G
x
y
O
Reaction Coordinate
O'
B'
B
(Cf)
D'
D
(Cm)
F
(Ci)
H
E(OH⁻)
E(O⁻)
E(O)
E(O2 vdw

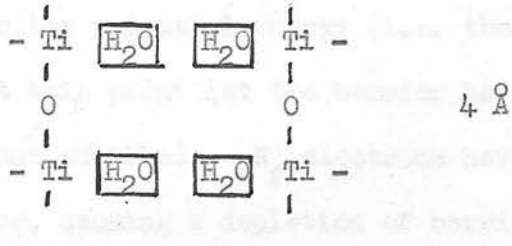
BOUNDARY LAYER THEORY OF CHEMISORPTION (37)

The number of sites on the surface of one gram of Sample II was approximately 170×10^{-6} N; where N is avogadros number (6.023×10^{23}).

i.e. No. of sites/gm. = 1.02×10^{20}

and the number of impurity centres/gm. = 4.1×10^{20}

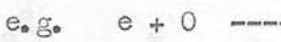
Taking the surface area of a site to be 20Å^2:-



the covering area of $1.02 + 10^{20}$ sites/g. will be $20 m^2/g.$ which is approximately 6% of the total surface area (= 350 $m^2/g.$)

The suggestion that depletive chemisorption on semiconductors might be treated purely as an electronic boundary layer problem was first put forward in 1952 by Aigrain and Dugas (48), Hauffe and Engell(49) and Weisz (50). In the case of cationic chemisorption on an n-type semiconductor (see Fig.54) the energy of the first atom will be $(\alpha - \varphi)e$, where α is the electron affinity of the adatom and φ the work function of the semiconductor since this is the energy change suffered by an electron in passing from a semi-:conductor to adsorbate, i.e. in this case:-

As more atoms are adsorbed and more electrons are transferred:-



the impurity centres are called upon to yield their electrons and the space /

space charge builds up in the boundary layer. As a result the potential energy of electrons in the semiconductor becomes modified and in passing from the semiconductor to chemisorbate electrons have to surmount a potential barrier V. Every atom adsorbed increases the height of this barrier by still further depressing the Fermi level in the semiconductor. Finally equilibrium is established when the potential energy of electrons in the adsorbate equals the potential energy (i.e. the Fermi Level), in the semi-:conductor. At this point let the barrier have a height V_f and let N_f be the number of ions adsorbed. N_f electrons have then been transferred from the semiconductor, causing a depletion of carriers in a boundary layer of depth $\underline{l}$. The assumption that the space charge desity ρ is constant in a boundary layer of thickness$\underline{l}$, but falls to zero deeper in the semiconductor, implies that every impurity centre in the boundary layer has given up its electrons to the chemisorbate. Also, it is assumed that the water in the hydroxyl ion vacancy is not mobile and that complete dissociation has occurred:-

$$- \overset{|}{\underset{|}{Ti}} \boxed{H_2O} \xrightarrow{\text{light}} - \overset{|}{\underset{|}{Ti}} - OH + H^+ + e$$

With these assumptions the value of ρ in the boundary layer will be -

$$\rho = - n_o e \qquad (24)$$

when n_o is the concentration of electrons which existed in the boundary layer before chemisorption.

By applying Poisson's equation, where $\varkappa$ is the dielectric constant of the semiconductor:-

$$\frac{d^2V}{dx^2} = - \frac{4\pi}{\varkappa} \rho \qquad (25)$$

Substituting from equation 24, intergration of 25 gives:-

V/

explained by the following theoretical treatment based on that given for H_2 on Ni films by Gundry and Thompkins (51). Oxygen in the gas phase must be in equilibrium with oxygen adsorbed on the surface (Van der Waals adsorption forces) as molecules and atoms:-

$$\underset{\text{gas}}{O_2} \underset{}{\overset{k}{\rightleftharpoons}} \underset{\text{surface}}{O_2} \overset{K}{\rightleftharpoons} \underset{\text{surface}}{2(O)\text{rapid}}$$

this process is reversible. Electrons produced from the impurity centres will cause the formation of O^- :-

$$O + e \xrightarrow{K_1} O^- \quad \text{slow} \qquad (32)$$

which will exist in a certain equilibrium concentration. Production of excess O^- will result in:-

$$O^- + H^+ \longrightarrow OH \text{ rapid} \qquad (33)$$

which can then accept further electrons to give an equilibrium concentration of OH^-:-

$$OH + e \xrightarrow{K_2} OH^- \text{ slow} \qquad (34)$$

The final stage will be:-

$$2\,OH^- + 2\,H^+ \longrightarrow 2\,H_2O \text{ rapid} \qquad (35)$$

Illustrating this on a potential energy diagram (Fig.55) it is seen that $E(O_2)_{vdw} < E(O) < E(O-) < E(OH-)$ and the slopes of GH< EF< CD< AB. represents the initial state where oxygen atoms are in dissociative equilibrium with oxygen molecules attracted to the surface by Van der Waals attractive forces. C_m is the intermediate state where oxygen has accepted an /

an electron to give a negatively charged ion. The final state C_f represents negatively charged OH groups. The full lines represent the titanium dioxide at the instant of illumination in oxygen. Transitions can occur from the Ci state to the C_m and C_f states without much activation energy and this has occasionally been observed. A direct transition from the C_i state to the C_f state requires a high activation energy.

With increasing sorption the heat of chemisorption decreases and the potential energy plots at a higher ΔO_2 value move to positions indicated in Fig. 55 by the short lines. When X and Y reach OO' an enthalpy of activation is required for the slow processes which then virually commences. This enthalpy increases with further sorption as adions pass from the C_m state to the C_f state. The concentrations of $[O^-]$ and $[OH^-]$ are given as good approximations by:-

$$[O^-]_{C_m} = K\sqrt{p_{O_2}} \exp\left(\frac{-\Delta F_1}{2RT}\right) \qquad (36a)$$

and

$$[OH^-]_{C_f} = K\sqrt{p_{O_2}} \exp\left(\frac{-\Delta F_2}{2RT}\right) \qquad (36b)$$

since a dissociative type of adsorption is envisaged the concentration of oxygen atoms and ions will be proportional to:- $\sqrt{p_{O_2}}$ (Henries Law).

ΔF_1 and ΔF_2 are the free energy differences between oxygen at P mm. and T^oA and adions O^- and OH^- in the C_m and C_f states. K is independant of P mm. and T^oA. The rates of the slow processes are then:-

$$\frac{d\Delta O_2}{dt} = KK_1\sqrt{P_{O_2}} \exp_e\left(\frac{-\Delta F_1}{2RT}\right)\exp_e\left(\frac{-E_1\ (\Delta O_2)_1}{RT}\right) \qquad (35a)$$

and /

and $$\frac{d\Delta O_2}{dt} = KK_2 \sqrt{P_{O_2}} \cdot \exp_e\left(\frac{-\Delta F_2}{2RT}\right) \cdot \exp_e\left(\frac{-E_2 (\Delta O_2)_2}{RT}\right) \qquad (35b)$$

where $E_1 (\Delta O_2)_1$ and $E_2(\Delta O_2)_2$ are the free energies of activation to pass from the C_i state to the C_m state and from the C_m state to the C_f state. Since the relevant sections of the plots B'X - XD' and D'Y - YF' are almost linear, the rise of B to B' and D to D' cause enthalpies of activation, $E_1(\Delta O_2)_1$ and $E_2(\Delta O_2)_2$ to rise accordingly to:-

$$E_1(\Delta O_2)_1 = -C_1 \left\{ (\Delta O_2)_1 - \Delta O_2 \right\} \qquad (38a)$$

$$E_2(\Delta O_2)_2 = -C_2 \left\{ (\Delta O_2)_2 - \Delta O_2 \right\} \qquad (38b)$$

where $(\Delta O_2)_1$ and $(\Delta O_2)_2$ are the maximum values of ΔO_2 for $E(\Delta O_2)_1$ and $E(\Delta O_2)_2 > 0$ and C_1 and C_2 are constants. Substitution of $E_1 (\Delta O_2)_1$ and $E_2(\Delta O_2)_2$ in equations (35a) and (35b) give:-

$$\frac{d\Delta O_2}{dt} = KK_1 \sqrt{P_{O_2}} \cdot \exp_e\left(\frac{-\Delta F_1}{2RT}\right) \cdot \exp\left(\frac{-C_1 \left\{ (\Delta O_2)_1 - \Delta O_2 \right\}}{RT}\right) \qquad (39a)$$

$$\frac{d\Delta O_2}{dt} = KK_2 \sqrt{P_{O_2}} \cdot \exp_e\left(\frac{-\Delta F_2}{2RT}\right) \cdot \exp_e\left(\frac{-C_2 \left\{ (\Delta O_2)_2 - \Delta O_2 \right\}}{RT}\right) \qquad (39b)$$

during the initial stages of the uptake the change in P_{O_2} is negligibly small and $\sqrt{P_{O_2}}$ may be taken as constant.

$$\therefore \log \frac{d\Delta O_2}{dt} = K_1' \left\{ (\Delta O_2)_1 - \Delta O_2 \right\} \qquad (40a)$$

and $$\log \frac{d\Delta O_2}{dt} = K_2' \left\{ (\Delta O_2)_2 - \Delta O_2 \right\} \qquad (40b)$$

showing how the breaks in linearity in the Roginsky ~~and~~ Zeldowich plot could occur due to the formation of equilibrium surface concentrations of O^- and OH^- /

OH^- adions. The values of $(\Delta O_2)_1$ and $(\Delta O_2)_2$ were approximately 2 and 7 μ/gm. (p.44).

Following the build up of maximum concentrations of O^- and OH^- on the surface the subsequent relationship between the rate of uptake and the extent of the uptake is simple:-

$$\frac{d\Delta p}{dt} = K \left(\frac{\Delta_\infty p - \Delta p}{\Delta p} \right) \qquad (41)$$

In this relationship the quantities $\Delta_\infty p$ and Δp are directly equivalent to the total number of sites initially present (n_o) and the total ammount oxidised (n) since oxygen is removed directly from the gas phase as molecules and only dissociates after sorption.

$$\frac{dn}{dt} = K \left(\frac{n_o - n}{n} \right) \qquad (42)$$

This reaction is characteristic of a simple first order process, tending towards an equilibrium where the velocity of oxidation $(\frac{dn}{dt})$ of sites $(n_o - n)$ is being retarded by the sites oxidised (n).

The kinetics of the oxidation of chemisorbed ammonia differs in that the relationship observed is:-

$$\frac{d\Delta p}{dt} = K \left(\frac{\sqrt{\Delta_\infty p} - \sqrt{\Delta p}}{\sqrt{\Delta p}} \right) \quad (\text{where } \Delta p = \Delta O_2)$$

and is taken to indicate, in this case, a direct dissociative adsorption:-

$$O_2 \text{ gas} \rightleftharpoons 2\ O \text{ surface}$$

and that the reaction stems from surface adsorbed oxygen atoms.

CONCLUSION

The foregoing discussion has established the photochemical reactions of titanium dioxide to occur on the surface. Although the postulated nature of the "photo-activated" surface has successfully explained the observed reactions it still remains to be further established. Study of the adsorption of un-:saturated hydrocarbons, in particular acetylene and ethylene, and other simple organic molecules such as formaldehyde and acetaldehyde might yield interesting results.

The problem of preventing photochemical properties in commercial titanium dioxide pigments still remains to be solved. It was not possible during the present work to determine whether they sponsored the same photo processes. If, however, theydo, then it is obvious that the pigment must, in some way,be prevented from having oxygen or hydroxyl deficiencies on the surface. It would be interesting to see if phosphine (PH_3) would displace waters in the same manner as ammonia and if it did, whether the subsequent uptake of oxygen would be photo or thermal.

Possible uses of titanium dioxide as a specific catalyst may arise from the proton donating and accepting properties resulting from the ammonia displacement of water, e.g. would it be possible to hydrogenate ethylene by illumination of hydrogen and ethylene? By working at elevated temperatures it might be possible to accomplish this thermally.

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